

Supporting Information for: Multi-phase halogen chemistry in the tropical Atlantic Ocean

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1 MISTRA v7.4.1

The MISTRA model is a one-dimensional model of the marine boundary layer (MBL). The model includes a description of meteorological and microphysical processes in the MBL and is described in detail in von Glasow et al. (2002a,b). The model includes explicit gas-phase and aqueous-phase chemical mechanisms, with particular focus on halogen chemistry. In this work, MISTRA version 7.4.1

was used; it includes minor improvements and bug fixes over version 7.3 (Pechtl and von Glasow, 2007; Pechtl et al., 2007). In particular, the gas-phase mechanism – shown in Tab. S3 – was upgraded as described below.

The gas-phase inorganic chemical mechanism was updated to the latest IUPAC and JPL recommendations (Atkinson et al., 2006; Sander et al., 2006) and the iodine mechanism was updated to the version presented in Sommariva et al. (2012). The chemistry of hydrocarbons and halogenated hydrocarbons – C2 species only – was revised by including more explicit treatment of the intermediates, such as peroxy radicals, based upon the Master Chemical Mechanism protocol (Saunders et al., 2003); this resulted in a more accurate description of ethane, ethene, formaldehyde, acetaldehyde, methanol and ethanol chemistry. The dimethyl sulphide (DMS) mechanism was also modified based on the review by Barnes et al. (2006). The aqueous-phase mechanism was the same as in (Pechtl and von Glasow, 2007; Pechtl et al., 2007).

MISTRA was run with a vertical resolution of 150 layers: the lowest 100 layers were each 12 m high, while the top 50 layers were spaced logarithmically to a maximum height of 2000 m. The chemical and meteorological initialization procedure and the setup of the model scenarios are described in the main text and were based on published observations of the marine boundary layer in the study region (see section Methods and cited references in the main paper).

The model was integrated using the KPP kinetic preprocessor version 1.3 (<http://people.cs.vt.edu/~asandu/Software/Kpp/>, Damian et al. (2002)). The model was run in Lagrangian mode, i.e., following the trajectory of an air mass. The first two days of the simulation were used to spin-up and initialize the model; therefore, they were discarded from the analysis of the results, which was focused on the third and fourth days of the simulation.

Species	γ
O ₃	6.60×10^{-6}
H ₂ O ₂	9.42×10^{-4}
NO ₂	8.90×10^{-9}
NO ₃	1.20×10^{-2}
HNO ₃	1.00×10^{-1}
N ₂ O ₅	1.30×10^{-2}
SO ₂	6.40×10^{-5}
HCOOH	2.30×10^{-5}

Table S1: Uptake coefficients of gas-phase species on Saharan dust (Atkinson et al., 2006) used in the DUST test case.

Species	Technique	Location/Platform	Reference
HCl, Cl*	tandem mist-chamber samplers	R/V Polarstern, CVAO	Keene et al. (2009); Lawler et al. (2009)
Cl ₂ , HOCl, BrCl	atmospheric pressure chemical ionization tandem mass spectrometry (APCI/MS/MS)	CVAO	Lawler et al. (2009, 2011)
BrO	long-path differential optical absorption spectroscopy (LP-DOAS)	CVAO	Read et al. (2008); Mahajan et al. (2010)
BrO	multi-axis differential optical absorption spectroscopy (MAX-DOAS)	R/V Polarstern, FS Poseidon	Leser et al. (2003); Martin et al. (2009)
Br _{inorg}	tandem mist-chamber samplers	R/V Polarstern	Keene et al. (2009)
IO	long-path differential optical absorption spectroscopy (LP-DOAS)	CVAO	Read et al. (2008); Mahajan et al. (2010)
Cl ⁻ (sub- & super-micron aerosol)	multi-stage impactors	RRS Discovery, CVAO	Allan et al. (2009); Müller et al. (2010)
Cl ⁻ (bulk aerosol)	multi-stage impactors	R/V Polarstern	Keene et al. (2009)
Br ⁻ (bulk aerosol)	multi-stage impactors	RRS Discovery, R/V Polarstern, CVAO	Allan et al. (2009); Keene et al. (2009); Müller et al. (2010)
IO ₃ ⁻ , I ⁻ (sub- & super-micron aerosol)	3-stage cascade impactors	R/V Meteor, RRS James Clark Ross, RRS Discovery	Baker (2004, 2005); Allan et al. (2009)

Table S2: Measurements of gas-phase and aqueous-phase halogen species in the tropical Atlantic Ocean. CVAO is the Cape Verde Atmospheric Observatory (São Vicente, Republic of Cape Verde).

Cl* $\simeq 2 \times \text{Cl}_2 + \text{HOCl}$.

Br_{inorg} = HBr + HOBr + BrNO₂ + BrNO₃ + 2 \times Br₂ + 2 \times Br₂O + Br + BrO + BrCl + IBr.

Table S3: Gas phase chemical mechanism in MISTRA v7.4.1.

no	reaction	n	A [(cm ⁻³) ¹⁻ⁿ s ⁻¹]	$-E_a / R$ [K]	reference
O1	O ¹ D + O ₂ → O ³ P	2	3.2×10^{-11}	67	Atkinson et al. (2006)
O2	O ¹ D + O ₃ → O ³ P + 1.5 O ₂	2	2.4×10^{-10}		Atkinson et al. (2006)
O3	O ¹ D + N ₂ → O ³ P	2	2.1×10^{-11}	115	Ravishankara et al. (2002)
O4	O ¹ D + H ₂ O → 2 OH	2	2.2×10^{-10}		Atkinson et al. (2006)
O5	O ¹ D + H ₂ + O ₂ → OH + HO ₂	2	1.2×10^{-10}	-2000	Atkinson et al. (2006)
O6	O ³ P + H ₂ O ₂ → OH + HO ₂	2	1.4×10^{-12}		Atkinson et al. (2006)
O7	O ³ P + O ₂ + O ₂ → O ₃ + O ₂	3	$6.0 \times 10^{-34} \times (T/300)^{-2.6}$	-2060	Atkinson et al. (2006)
O8	O ³ P + O ₃ → 2 O ₂	2	8.0×10^{-12}		Atkinson et al. (2006)
O9	O ³ P + O ₂ + N ₂ → O ₃ + N ₂	3	$5.6 \times 10^{-34} \times (T/300)^{-2.6}$		Atkinson et al. (2006)
O10	OH + O ₃ → HO ₂ + O ₂	2	1.7×10^{-12}	-940	Atkinson et al. (2006)
O11	OH + HO ₂ → H ₂ O + O ₂	2	4.8×10^{-11}	250	Atkinson et al. (2006)
O12	OH + H ₂ + O ₂ → HO ₂ + H ₂ O	2	7.7×10^{-12}	-2100	Atkinson et al. (2006)
O13	OH + H ₂ O ₂ → HO ₂ + H ₂ O	2	2.9×10^{-12}	-160	Atkinson et al. (2006)
O14	OH + OH → O ³ P + H ₂ O	2	$6.2 \times 10^{-14} \times (T/298)^{2.6}$	945	Atkinson et al. (2006)
O15	OH + OH + M → H ₂ O ₂	3	†		Atkinson et al. (2006)
O16	HO ₂ + O ₃ → OH + 2 O ₂	2	$2.03 \times 10^{-16} \times (T/300)^{4.57}$	693	Atkinson et al. (2006)
O17	HO ₂ + HO ₂ → H ₂ O ₂ + O ₂	2	†		Atkinson et al. (2006)
O18	O ₃ + hν → O ₂ + O ¹ D	1	§		Atkinson et al. (2006)
O19	O ₃ + hν → O ₂ + O ³ P	1	§		Atkinson et al. (2006)
O20	H ₂ O ₂ + hν → 2 OH	1	§		Atkinson et al. (2006)
N01	NO + O ³ P + M → NO ₂	3	†		Atkinson et al. (2006)
N02	NO + OH + M → HONO	3	†		Atkinson et al. (2006)
N03	NO + HO ₂ → NO ₂ + OH	2	3.6×10^{-12}	270	Atkinson et al. (2006)
N04	NO + O ₃ → NO ₂ + O ₂	2	1.4×10^{-12}	-1310	Atkinson et al. (2006)
N05	NO + NO ₃ → 2 NO ₂	2	1.8×10^{-11}	110	Atkinson et al. (2006)
N06	NO ₂ + O ³ P → NO + O ₂	2	5.5×10^{-12}	188	Atkinson et al. (2006)
N07	NO ₂ + O ³ P + M → NO ₃	3	†		Atkinson et al. (2006)
N08	NO ₂ + OH + M → HNO ₃	3	†		Atkinson et al. (2006)
N09	NO ₂ + HO ₂ + M → HNO ₄	3	†		Sander et al. (2006)
N10	NO ₂ + O ₃ → NO ₃ + O ₂	2	1.4×10^{-13}	-2470	Atkinson et al. (2006)

Table S3: continued.

no	reaction	n	$A [(\text{cm}^{-3})^{1-n} \text{s}^{-1}]$	$-E_a / R$ [K]	reference
N11	$\text{NO}_2 + \text{NO}_3 + \text{M} \rightarrow \text{N}_2\text{O}_5$	3	†		Sander et al. (2006)
N13	$\text{NO}_2 + \text{h}\nu \rightarrow \text{NO} + \text{O}^3\text{P}$	1	§		
N14	$\text{NO}_3 + \text{O}^3\text{P} \rightarrow \text{NO}_2 + \text{O}_2$	2	1.7×10^{-11}		Atkinson et al. (2006)
N15	$\text{NO}_3 + \text{OH} \rightarrow \text{HO}_2 + \text{NO}_2$	2	2.0×10^{-11}		Atkinson et al. (2006)
N16	$\text{NO}_3 + \text{HO}_2 \rightarrow \text{OH} + \text{NO}_2 + \text{O}_2$	2	4.0×10^{-12}		Atkinson et al. (2006)
N17	$\text{NO}_3 + \text{NO}_3 \rightarrow \text{NO}_2 + \text{NO}_2 + \text{O}_2$	2	8.5×10^{-13}	-2450	Sander et al. (2006)
N18	$\text{NO}_3 + \text{h}\nu \rightarrow \text{NO} + \text{O}_2$	1	§		
N19	$\text{NO}_3 + \text{h}\nu \rightarrow \text{NO}_2 + \text{O}^3\text{P}$	1	§		
N20	$\text{N}_2\text{O}_5 + \text{M} \rightarrow \text{NO}_2 + \text{NO}_3$	2	†		Osthoff et al. (2007)
N21	$\text{N}_2\text{O}_5 + \text{h}\nu \rightarrow \text{NO}_2 + \text{NO}_3$	1	§		
N24	$\text{HONO} + \text{OH} \rightarrow \text{NO}_2$	2	2.5×10^{-12}	260	Atkinson et al. (2006)
N25	$\text{HONO} + \text{h}\nu \rightarrow \text{NO} + \text{OH}$	1	§		
N26	$\text{HNO}_3 + \text{OH} \rightarrow \text{NO}_3 + \text{H}_2\text{O}$	2	†		Atkinson et al. (2006)
N27	$\text{HNO}_3 + \text{h}\nu \rightarrow \text{NO}_2 + \text{OH}$	1	§		
N28	$\text{HNO}_4 + \text{M} \rightarrow \text{NO}_2 + \text{HO}_2$	2	†		Sander et al. (2006)
N29	$\text{HNO}_4 + \text{OH} \rightarrow \text{NO}_2 + \text{H}_2\text{O} + \text{O}_2$	2	3.2×10^{-13}	690	Atkinson et al. (2006)
N30	$\text{HNO}_4 + \text{h}\nu \rightarrow \text{NO}_2 + \text{HO}_2$	1	§		
N31	$\text{HNO}_4 + \text{h}\nu \rightarrow \text{OH} + \text{NO}_3$	1	§		
N32	$\text{NH}_3 + \text{OH} \rightarrow \text{NHS} + \text{H}_2\text{O}$	2	3.5×10^{-12}	-925	Atkinson et al. (2006)
C01	$\text{CO} + \text{OH} \rightarrow \text{HO}_2 + \text{CO}_2$	2	†		Atkinson et al. (2006)
C02	$\text{CH}_4 + \text{OH} \rightarrow \text{MO}_2 + \text{H}_2\text{O}$	2	$1.85 \times 10^{-20} \times (T)^{2.82}$	-987	Atkinson and Arey (2003)
C03	$\text{C}_2\text{H}_6 + \text{OH} \rightarrow \text{ETO}_2 + \text{H}_2\text{O}$	2	$1.49 \times 10^{-17} \times (T)^2$	-499	Atkinson and Arey (2003)
C04	$\text{ETHE} + \text{OH} + \text{O}_2 \rightarrow \text{EO}_2$	2	†		Atkinson and Arey (2003)
C05	$\text{ETHE} + \text{O}_3 \rightarrow \text{HCHO} + 0.63 \text{ CO} + 0.13 \text{ HO}_2 + 0.13 \text{ OH} + 0.37 \text{ CHO}_2$	2	9.14×10^{-15}	-2580	Atkinson and Arey (2003)
C06	$\text{ETHE} + \text{NO}_3 + \text{O}_2 \rightarrow \text{EO}_2$	2	$4.88 \times 10^{-18} \times (T)^2$	-2282	Atkinson and Arey (2003)
C07	$\text{CHO}_2 + \text{H}_2\text{O} \rightarrow \text{ACO}_2$	2	1.0×10^{-17}		MCM *
C08	$\text{MO}_2 + \text{NO} + \text{O}_2 \rightarrow \text{HCHO} + \text{HO}_2 + \text{NO}_2$	2	$2.8 \times 10^{-12} \times 0.999$	300	Tyndall et al. (2001)
C09	$\text{MO}_2 + \text{HO}_2 \rightarrow \text{ROOH} + \text{O}_2$	2	4.15×10^{-13}	750	Tyndall et al. (2001)
C10	$\text{MO}_2 + \text{MO}_2 \rightarrow \text{CH}_3\text{OH} + \text{HCHO} + \text{O}_2$	2	$9.5 \times 10^{-14} \times 0.63$	390	Tyndall et al. (2001)

Table S3: continued.

no	reaction	n	$A [(\text{cm}^{-3})^{1-n} \text{s}^{-1}]$	$-E_a / R$ [K]	reference
C11	$\text{MO}_2 + \text{MO}_2 \longrightarrow 2 \text{HCHO} + 2 \text{HO}_2$	2	$9.5 \times 10^{-14} \times 0.37$	390	Tyndall et al. (2001)
C12	$\text{ETO}_2 + \text{NO} \longrightarrow \text{ALD2} + \text{HO}_2 + \text{NO}_2$	2	$2.6 \times 10^{-12} \times 0.991$	365	MCM *
C13	$\text{ETO}_2 + \text{HO}_2 \longrightarrow \text{ROOH} + \text{O}_2$	2	2.7×10^{-13}	1000	MCM *
C14	$\text{ETO}_2 + \text{ETO}_2 \longrightarrow \text{C}_2\text{H}_5\text{OH} + \text{ALD2} + \text{O}_2$	2	$3.10 \times 10^{-13} \times 0.4$		MCM *
C15	$\text{ETO}_2 + \text{ETO}_2 \longrightarrow 2 \text{ALD2} + 2 \text{HO}_2$	2	$3.10 \times 10^{-13} \times 0.6$		MCM *
C16	$\text{ETO}_2 + \text{MO}_2 \longrightarrow \text{ALD2} + \text{CH}_3\text{OH}$	2	$3.10 \times 10^{-13} \times 0.2$		MCM *
C17	$\text{ETO}_2 + \text{MO}_2 \longrightarrow \text{C}_2\text{H}_5\text{OH} + \text{HCHO}$	2	$3.10 \times 10^{-13} \times 0.2$		MCM *
C18	$\text{ETO}_2 + \text{MO}_2 \longrightarrow \text{HCHO} + \text{ALD2} + 2 \text{HO}_2$	2	$3.10 \times 10^{-13} \times 0.6$		MCM *
C19	$\text{EO}_2 + \text{NO} \longrightarrow \text{ALD2} + \text{HO}_2 + \text{NO}_2$	2	$2.54 \times 10^{-12} \times 0.33$	360	MCM *
C20	$\text{EO}_2 + \text{NO} \longrightarrow 2 \text{HCHO} + \text{HO}_2 + \text{NO}_2$	2	$2.54 \times 10^{-12} \times 0.66$	360	MCM *
C21	$\text{EO}_2 + \text{HO}_2 \longrightarrow \text{ROOH} + \text{O}_2$	2	2.0×10^{-13}	1250	MCM *
C22	$\text{EO}_2 + \text{EO}_2 \longrightarrow \text{C}_2\text{H}_5\text{OH} + \text{ALD2} + \text{O}_2$	2	$2.0 \times 10^{-12} \times 0.4$		MCM *
C23	$\text{EO}_2 + \text{EO}_2 \longrightarrow 2 \text{HCHO} + \text{ALD2} + 2 \text{HO}_2$	2	$2.0 \times 10^{-12} \times 0.6$		MCM *
C24	$\text{EO}_2 + \text{MO}_2 \longrightarrow \text{C}_2\text{H}_5\text{OH} + \text{HCHO}$	2	$2.0 \times 10^{-12} \times 0.2$		MCM *
C25	$\text{EO}_2 + \text{MO}_2 \longrightarrow \text{ALD2} + \text{CH}_3\text{OH}$	2	$2.0 \times 10^{-12} \times 0.2$		MCM *
C26	$\text{EO}_2 + \text{MO}_2 \longrightarrow 2 \text{HCHO} + 0.5 \text{ALD2} + 2 \text{HO}_2$	2	$2.0 \times 10^{-12} \times 0.6$		MCM *
C27	$\text{MCO}_3 + \text{NO} + \text{O}_2 \longrightarrow \text{MO}_2 + \text{NO}_2$	2	8.1×10^{-12}	270	Tyndall et al. (2001)
C28	$\text{MCO}_3 + \text{HO}_2 \longrightarrow \text{ROOH} + \text{O}_2$	2	4.3×10^{-13}	1040	Tyndall et al. (2001)
C29	$\text{MCO}_3 + \text{MCO}_3 \longrightarrow 2 \text{MO}_2$	2	2.5×10^{-12}	500	Tyndall et al. (2001)
C30	$\text{MCO}_3 + \text{MO}_2 \longrightarrow \text{MO}_2 + \text{HO}_2 + \text{HCHO}$	2	$2.0 \times 10^{-12} \times 0.9$	500	Tyndall et al. (2001)
C31	$\text{MCO}_3 + \text{MO}_2 \longrightarrow \text{ACTA} + \text{HCHO}$	2	$2.0 \times 10^{-12} \times 0.1$	500	Tyndall et al. (2001)
C32	$\text{MCO}_3 + \text{NO}_2 + \text{M} \longrightarrow \text{PAN}$	3	†		Sander et al. (2006)
C33	$\text{PAN} + \text{M} \longrightarrow \text{MCO}_3 + \text{NO}_2$	2	†		Sander et al. (2006)
C34	$\text{PAN} + \text{OH} \longrightarrow \text{HCHO} + \text{CO} + \text{NO}_2$	2	9.5×10^{-13}	-650	MCM *
C35	$\text{HCHO} + \text{OH} \longrightarrow \text{HO}_2 + \text{CO} + \text{H}_2\text{O}$	2	1.2×10^{-14}	287	Atkinson and Arey (2003)
C36	$\text{HCHO} + \text{NO}_3 \longrightarrow \text{HNO}_3 + \text{HO}_2 + \text{CO}$	2	5.6×10^{-16}		Atkinson and Arey (2003)
C37	$\text{HCHO} + \text{h}\nu \longrightarrow 2 \text{HO}_2 + \text{CO}$	1	§		
C38	$\text{HCHO} + \text{h}\nu \longrightarrow \text{CO} + \text{H}_2$	1	§		

Table S3: continued.

no	reaction	n	$A [(\text{cm}^{-3})^{1-n} \text{s}^{-1}]$	$-E_a / R [\text{K}]$	reference
C39	ALD2 + OH \longrightarrow MCO ₃ + H ₂ O	2	4.4×10^{-12}	365	Atkinson and Arey (2003)
C40	ALD2 + NO ₃ \longrightarrow HNO ₃ + MCO ₃	2	1.4×10^{-12}	-1860	Atkinson and Arey (2003)
C41	ALD2 + hv \longrightarrow MO ₂ + HO ₂ + CO	1	\S		
C42	CH ₃ OH + OH \longrightarrow HO ₂ + HCHO	2	$6.0 \times 10^{-18} \times (T)^2$	170	Atkinson and Arey (2003)
C43	C ₂ H ₅ OH + OH \longrightarrow EO ₂	2	$6.1 \times 10^{-18} \times (T)^2 \times 0.11$	530	Atkinson and Arey (2003)
C44	C ₂ H ₅ OH + OH \longrightarrow ALD2 + HO ₂	2	$6.1 \times 10^{-18} \times (T)^2 \times 0.89$	530	Atkinson and Arey (2003)
C45	ACO ₂ + OH \longrightarrow HO ₂ + H ₂ O + CO ₂	2	4.5×10^{-13}		MCM *
C46	ACTA + OH \longrightarrow MO ₂ + H ₂ O + CO ₂	2	8.0×10^{-13}		MCM *
C47	ROOH + OH \longrightarrow MO ₂ + H ₂ O	2	1.9×10^{-12}	190	MCM *
C48	ROOH + OH \longrightarrow HCHO + OH	2	1.0×10^{-12}	190	MCM *
C49	ROOH + hv \longrightarrow HCHO + OH + HO ₂	1	\S		
C50	MO ₂ + NO \longrightarrow RAN1	2	$2.8 \times 10^{-12} \times 0.001$	300	Tyndall et al. (2001)
C51	ETO ₂ + NO \longrightarrow RAN1	2	$2.6 \times 10^{-12} \times 0.009$	365	MCM *
C52	RAN1 + OH \longrightarrow HCHO + NO ₂	2	1.0×10^{-14}	1060	MCM *
C53	RAN1 + hv \longrightarrow HCHO + HO ₂ + NO ₂	1	\S		
S1	SO ₂ + O ³ P + M \longrightarrow SO ₃	3	4.0×10^{-32}	-1000	Atkinson et al. (2006)
S2	SO ₂ + OH + M \longrightarrow HOSO ₂	3	\dagger		Atkinson et al. (2006)
S3	SO ₂ + O ₃ \longrightarrow SO ₃ + O ₂	2	3.0×10^{-12}	-7000	Sander et al. (2006)
S3	HOSO ₂ + O ₂ \longrightarrow HO ₂ + SO ₃	2	1.3×10^{-12}	-330	Atkinson et al. (2006)
S4	SO ₃ + 2 H ₂ O \longrightarrow H ₂ SO ₄	1	$3.9 \times 10^{-41} \times 3.626 \times 10^{35} \times [\text{H}_2\text{O}]^2$	6893	Atkinson et al. (2006)
S5	SO ₃ + NH ₃ + M \longrightarrow NHS	3	2.0×10^{-11}		Atkinson et al. (2006)
D01	DMS + OH + O ₂ \longrightarrow DMOO + H ₂ O	2	1.12×10^{-11}	-250	Atkinson et al. (2006)
D02	DMS + OH + O ₂ \longrightarrow DMSO + HO ₂	2	\dagger		Atkinson et al. (2006)
D04	DMS + NO ₃ + O ₂ \longrightarrow DMOO + HNO ₃	2	1.9×10^{-13}	520	Atkinson et al. (2006)
D05	DMS + Cl + O ₂ \longrightarrow 0.45 DMOO + 0.45 HCl + 0.55 DMSO + 0.55 ClO	2	3.4×10^{-13}	2081	Atkinson et al. (2006)
D06	DMS + Br + O ₂ \longrightarrow MO ₂ + RBr	2	9.0×10^{-11}	-2386	Jefferson et al. (1994)
D07	DMS + ClO \longrightarrow DMSO + Cl	2	1.7×10^{-15}	340	Atkinson et al. (2006)
D08	DMS + BrO \longrightarrow DMSO + Br	2	1.5×10^{-14}	1000	Atkinson et al. (2006)
D09	DMS + IO \longrightarrow DMSO + I	2	3.3×10^{-13}	-925	Atkinson et al. (2006)

Table S3: continued.

no	reaction	n	$A [(\text{cm}^{-3})^{1-n} \text{s}^{-1}]$	$-E_a / R [\text{K}]$	reference
D10	$\text{DMOO} + \text{NO} \longrightarrow \text{HCHO} + \text{CH}_3\text{S} + \text{NO}_2$	2	4.9×10^{-12}	260	Atkinson et al. (2006)
D11	$\text{DMOO} + \text{HO}_2 \longrightarrow \text{SOR}$	2	5.0×10^{-12}		Barnes et al. (2006)
D12	$\text{DMOO} + \text{DMOO} \longrightarrow 2 \text{HCHO} + 2 \text{CH}_3\text{S} + \text{O}_2$	2	1.0×10^{-11}		Atkinson et al. (2006)
D13	$\text{DMOO} + \text{MO}_2 \longrightarrow \text{CH}_3\text{S} + 2 \text{HCHO} + \text{HO}_2$	2	3.10×10^{-13}		MCM *
D14	$\text{DMOO} + \text{NO}_2 \longrightarrow \text{SPAN}$	2	9.0×10^{-12}		Atkinson et al. (2006)
D15	$\text{CH}_3\text{S} + \text{O}_3 \longrightarrow \text{CH}_3\text{SO} + \text{O}_2$	2	1.15×10^{-12}	432	Atkinson et al. (2006)
D16	$\text{CH}_3\text{S} + \text{NO}_2 \longrightarrow \text{CH}_3\text{SO} + \text{NO}$	2	3.0×10^{-11}	210	Atkinson et al. (2006)
D17	$\text{CH}_3\text{S} + \text{NO}_2 + \text{O}_2 \longrightarrow \text{SPAN}$	2	2.2×10^{-11}		Atkinson et al. (2006)
D18	$\text{CH}_3\text{S} + \text{NO} + \text{O}_2 \longrightarrow \text{CH}_3\text{SO} + \text{NO}_2$	2	1.1×10^{-11}		Atkinson et al. (2006)
D19	$\text{CH}_3\text{S} + \text{NO} \longrightarrow \text{NHS}$	2	9.0×10^{-12}		Turnipseed et al. (1996)
D20	$\text{CH}_3\text{SO} + \text{O}_3 \longrightarrow \text{CH}_3\text{SO}_2 + \text{O}_2$	2	4.1×10^{-13}		Atkinson et al. (2006)
D21	$\text{CH}_3\text{SO} + \text{NO}_2 \longrightarrow \text{CH}_3\text{SO}_2 + \text{NO}$	2	$1.2 \times 10^{-11} \times 0.75$		Turnipseed et al. (1996)
D22	$\text{CH}_3\text{SO} + \text{NO}_2 \longrightarrow \text{SO}_2 + \text{MO}_2 + \text{NO}$	2	$1.2 \times 10^{-11} \times 0.25$		Atkinson et al. (2006)
D23	$\text{CH}_3\text{SO}_2 + \text{M} \longrightarrow \text{MO}_2 + \text{SO}_2$	2	1.36×10^{14}	-8656	Barnes et al. (2006)
D24	$\text{CH}_3\text{SO}_2 + \text{O}_3 \longrightarrow \text{CH}_3\text{SO}_3 + \text{O}_2$	2	5.0×10^{-15}		Atkinson et al. (2006)
D25	$\text{CH}_3\text{SO}_2 + \text{NO}_2 \longrightarrow \text{CH}_3\text{SO}_3 + \text{NO}$	2	1.0×10^{-15}		Barnes et al. (2006)
D26	$\text{CH}_3\text{SO}_2 + \text{NO}_2 + \text{O}_2 \longrightarrow \text{SPAN}$	2	1.0×10^{-12}		Barnes et al. (2006)
D27	$\text{CH}_3\text{SO}_2 + \text{NO} + \text{O}_2 \longrightarrow \text{CH}_3\text{SO}_3 + \text{NO}$	2	1.0×10^{-11}		Barnes et al. (2006)
D28	$\text{CH}_3\text{SO}_3 + \text{HO}_2 \longrightarrow \text{CH}_3\text{SO}_3\text{H} + \text{O}_2$	2	5.0×10^{-11}		Barnes et al. (2006)
D30	$\text{SOR} + \text{OH} \longrightarrow \text{DMOO} + \text{H}_2\text{O}$	2	2.9×10^{-12}	190	MCM *
D31	$\text{SOR} + \text{h}\nu \longrightarrow \text{CH}_3\text{S} + \text{HCHO} + \text{OH}$	1	§		
D32	$\text{SPAN} \longrightarrow \text{CH}_3\text{SO}_2 + \text{NO}_2 + \text{O}_2$	1	2.7×10^{15}	99	Barnes et al. (2006)
D33	$\text{DMSO} + \text{OH} \longrightarrow 0.95 \text{CH}_3\text{SO}_2\text{H} + 0.95 \text{MO}_2 + 0.05 \text{DMSO}_2$	2	9.0×10^{-11}		Kukui et al. (2003)
D34	$\text{DMSO} + \text{Cl} \longrightarrow 0.9 \text{DMOO} + 0.9 \text{HCl} + 0.1 \text{CH}_3\text{SO} + 0.1 \text{MO}_2$	2	1.37×10^{-11}	709	Barnes et al. (2006)

Table S3: continued.

no	reaction	n	$A [(\text{cm}^{-3})^{-1} \text{s}^{-1}]$	$-E_a / R [\text{K}]$	reference
D35	$\text{DMSO} + \text{BrO} \longrightarrow \text{DMSO}_2 + \text{Br}$	2	1.0×10^{-14}		Ballesteros et al. (2002)
D36	$\text{CH}_3\text{SO}_2\text{H} + \text{OH} \longrightarrow 0.95 \text{CH}_3\text{SO}_2 + 0.05 \text{CH}_3\text{SO}_3\text{H} + 0.05 \text{HO}_2$	2	9.0×10^{-11}		Kukui et al. (2003)
D37	$\text{CH}_3\text{SO}_2\text{H} + \text{NO}_3 \longrightarrow \text{CH}_3\text{SO}_2 + \text{HNO}_3$	2	1.0×10^{-13}		Yin et al. (1990a,b)
Cl01	$\text{Cl} + \text{O}_3 \longrightarrow \text{ClO} + \text{O}_2$	2	2.8×10^{-11}	-250	Atkinson et al. (2006)
Cl02	$\text{Cl} + \text{HO}_2 \longrightarrow \text{HCl} + \text{O}_2$	2	$4.4 \times 10^{-11} \times (1 - 1.7 \times e^{(-620/T)})$		Atkinson et al. (2006)
Cl03	$\text{Cl} + \text{HO}_2 \longrightarrow \text{ClO} + \text{OH}$	2	$4.4 \times 10^{-11} \times (1.7 \times e^{(-620/T)})$		Atkinson et al. (2006)
Cl04	$\text{Cl} + \text{H}_2\text{O}_2 \longrightarrow \text{HCl} + \text{HO}_2$	2	1.1×10^{-11}	-980	Atkinson et al. (2006)
Cl05	$\text{Cl} + \text{H}_2 + \text{O}_2 \longrightarrow \text{HCl} + \text{HO}_2$	2	3.9×10^{-11}	-2310	Atkinson et al. (2006)
Cl06	$\text{Cl} + \text{HNO}_3 \longrightarrow \text{HCl} + \text{NO}_3$	2	2.0×10^{-16}		Atkinson et al. (2006)
Cl07	$\text{Cl} + \text{NO}_2 + \text{M} \longrightarrow \text{ClONO}$	3	\dagger		Sander et al. (2006)
Cl08	$\text{Cl} + \text{NO}_2 + \text{M} \longrightarrow \text{ClNO}_2$	3	\dagger		Sander et al. (2006)
Cl09	$\text{Cl} + \text{NO}_3 \longrightarrow \text{ClO} + \text{NO}_2$	2	2.4×10^{-11}		Atkinson et al. (2006)
Cl10	$\text{Cl}_2 + \text{OH} \longrightarrow \text{HOCl} + \text{Cl}$	2	3.6×10^{-12}	-1200	Atkinson et al. (2006)
Cl11	$\text{Cl}_2 + \text{h}\nu \longrightarrow 2 \text{Cl}$	1	\S		
Cl12	$\text{ClO} + \text{O}^3\text{P} \longrightarrow \text{Cl} + \text{O}_2$	2	2.5×10^{-11}	110	Atkinson et al. (2006)
Cl13	$\text{ClO} + \text{OH} \longrightarrow \text{Cl} + \text{HO}_2$	2	$7.3 \times 10^{-12} \times 0.94$	300	Atkinson et al. (2006)
Cl14	$\text{ClO} + \text{OH} \longrightarrow \text{HCl} + \text{O}_2$	2	$7.3 \times 10^{-12} \times 0.06$	300	Atkinson et al. (2006)
Cl15	$\text{ClO} + \text{HO}_2 \longrightarrow \text{HOCl} + \text{O}_2$	2	2.2×10^{-12}	340	Atkinson et al. (2006)
Cl16	$\text{ClO} + \text{O}_3 \longrightarrow \text{Cl} + 2 \text{O}_2$	2	1.5×10^{-17}		Atkinson et al. (2006)
Cl17	$\text{ClO} + \text{O}_3 \longrightarrow \text{OClO} + \text{O}_2$	2	1.0×10^{-18}		Atkinson et al. (2006)
Cl18	$\text{ClO} + \text{NO} \longrightarrow \text{Cl} + \text{NO}_2$	2	6.2×10^{-12}	295	Atkinson et al. (2006)
Cl19	$\text{ClO} + \text{NO}_2 + \text{M} \longrightarrow \text{ClONO}_2$	3	\dagger		Atkinson et al. (2006)
Cl20	$\text{ClO} + \text{NO}_3 \longrightarrow \text{Cl} + \text{NO}_2 + \text{O}_2$	2	$4.6 \times 10^{-13} \times 0.74$		Atkinson et al. (2006)
Cl21	$\text{ClO} + \text{NO}_3 \longrightarrow \text{OClO} + \text{NO}_2$	2	$4.6 \times 10^{-13} \times 0.26$		Atkinson et al. (2006)
Cl22	$\text{ClO} + \text{ClO} \longrightarrow \text{Cl}_2 + \text{O}_2$	2	1.0×10^{-12}	-1590	Atkinson et al. (2006)
Cl23	$\text{ClO} + \text{ClO} \longrightarrow 2 \text{Cl} + \text{O}_2$	2	3.0×10^{-11}	-2450	Atkinson et al. (2006)
Cl24	$\text{ClO} + \text{ClO} \longrightarrow \text{Cl} + \text{OClO}$	2	3.5×10^{-13}	-1370	Atkinson et al. (2006)
Cl25	$\text{ClO} + \text{ClO} + \text{M} \longrightarrow \text{Cl}_2\text{O}_2$	3	\dagger		Sander et al. (2006)
Cl27	$\text{ClO} + \text{OClO} + \text{M} \longrightarrow \text{Cl}_2\text{O}_3$	3	\dagger		Sander et al. (2006)

Table S3: continued.

no	reaction	n	$A [(\text{cm}^{-3})^{1-n} \text{s}^{-1}]$	$-E_a / R [\text{K}]$	reference
Cl28	$\text{OCIO} + \text{Cl} \rightarrow \text{ClO} + \text{ClO}$	2	3.2×10^{-11}	170	Atkinson et al. (2006)
Cl29	$\text{OCIO} + \text{O}^3\text{P} \rightarrow \text{ClO} + \text{O}_2$	2	2.4×10^{-12}	-960	Atkinson et al. (2006)
Cl30	$\text{OCIO} + \text{O}^3\text{P} + \text{M} \rightarrow \text{ClO}_3$	3	†		Atkinson et al. (2006)
Cl31	$\text{OCIO} + \text{OH} \rightarrow \text{HOCl} + \text{O}_2$	2	1.4×10^{-12}	600	Atkinson et al. (2006)
Cl32	$\text{OCIO} + \text{O}_3 \rightarrow \text{ClO}_3 + \text{O}_2$	2	2.1×10^{-12}	-4700	Atkinson et al. (2006)
Cl33	$\text{OCIO} + \text{NO} \rightarrow \text{ClO} + \text{NO}_2$	2	1.1×10^{-13}	350	Atkinson et al. (2006)
Cl34	$\text{OCIO} + \text{O}_2 + \text{hv} \rightarrow \text{O}_3 + \text{ClO}$	1	§		
Cl35	$\text{Cl}_2\text{O}_2 + \text{Cl} \rightarrow \text{Cl}_2 + \text{Cl} + \text{O}_2$	2	7.6×10^{-11}	65	Atkinson et al. (2006)
Cl36	$\text{Cl}_2\text{O}_2 + \text{O}_3 \rightarrow \text{ClO} + \text{Cl} + 2\text{O}_2$	2	1.0×10^{-19}		Atkinson et al. (2006)
Cl37	$\text{Cl}_2\text{O}_2 + \text{M} \rightarrow \text{ClO} + \text{ClO}$	2	†		Sander et al. (2006)
Cl38	$\text{Cl}_2\text{O}_2 + \text{hv} \rightarrow \text{Cl} + \text{Cl} + \text{O}_2$	1	§		
Cl39	$\text{Cl}_2\text{O}_3 + \text{M} \rightarrow \text{ClO} + \text{OCIO}$	2	†		Sander et al. (2006)
Cl40	$\text{HCl} + \text{OH} \rightarrow \text{H}_2\text{O} + \text{Cl}$	2	1.7×10^{-12}	-230	Atkinson et al. (2006)
Cl41	$\text{HOCl} + \text{O}^3\text{P} \rightarrow \text{ClO} + \text{OH}$	2	1.7×10^{-13}		Atkinson et al. (2006)
Cl42	$\text{HOCl} + \text{OH} \rightarrow \text{ClO} + \text{H}_2\text{O}$	2	3.0×10^{-12}	-500	Sander et al. (2006)
Cl43	$\text{HOCl} + \text{hv} \rightarrow \text{Cl} + \text{OH}$	1	§		
Cl44	$\text{ClNO}_2 + \text{OH} \rightarrow \text{HOCl} + \text{NO}_2$	2	2.4×10^{-12}	-1250	Atkinson et al. (2006)
Cl45	$\text{ClNO}_2 + \text{hv} \rightarrow \text{Cl} + \text{NO}_2$	1	§		
Cl46	$\text{ClNO}_3 + \text{Cl} \rightarrow \text{Cl}_2 + \text{NO}_3$	2	6.2×10^{-12}	145	Atkinson et al. (2006)
Cl47	$\text{ClNO}_3 + \text{O}^3\text{P} \rightarrow \text{ClO} + \text{NO}_3$	2	4.5×10^{-12}	-900	Atkinson et al. (2006)
Cl48	$\text{ClNO}_3 + \text{OH} \rightarrow 0.5 \text{ClO} + 0.5 \text{HNO}_3 + 0.5 \text{HOCl} + 0.5 \text{NO}_3$	2	1.2×10^{-12}	-330	Atkinson et al. (2006)
Cl49	$\text{ClNO}_3 + \text{M} \rightarrow \text{ClO} + \text{NO}_2$	2	†		Anderson and Fahey (1990)
Cl50	$\text{ClNO}_3 + \text{hv} \rightarrow \text{Cl} + \text{NO}_3$	1	§		
Cl51	$\text{Cl} + \text{CH}_4 + \text{O}_2 \rightarrow \text{HCl} + \text{MO}_2$	2	6.6×10^{-12}	-1240	Atkinson et al. (2006)
Cl52	$\text{Cl} + \text{C}_2\text{H}_6 + \text{O}_2 \rightarrow \text{HCl} + \text{ETO}_2$	2	8.3×10^{-11}	-100	Atkinson et al. (2006)
Cl53	$\text{Cl} + \text{ETHE} + \text{O}_2 \rightarrow \text{ClRO}_2$	2	†		Atkinson et al. (2006)
Cl54	$\text{Cl} + \text{HCHO} \rightarrow \text{HCl} + \text{HO}_2 + \text{CO}$	2	8.1×10^{-11}	-34	Atkinson et al. (2006)
Cl55	$\text{Cl} + \text{ALD2} \rightarrow \text{HCl} + \text{MCO}_3$	2	8.0×10^{-11}		Atkinson et al. (2006)
Cl56	$\text{Cl} + \text{CH}_3\text{OH} \rightarrow \text{HCl} + \text{HO}_2 + \text{HCHO}$	2	5.5×10^{-11}		Atkinson et al. (2006)

Table S3: continued.

no	reaction	n	$A [(\text{cm}^{-3})^{1-n} \text{s}^{-1}]$	$-E_a / R [\text{K}]$	reference
Cl57	$\text{Cl} + \text{C}_2\text{H}_5\text{OH} \longrightarrow \text{HCl} + 0.92 \text{ ALD2} + 0.92 \text{ HO}_2 + 0.08 \text{ EO}_2$	2	8.6×10^{-11}	45	Atkinson et al. (2006)
Cl58	$\text{Cl} + \text{ROOH} \longrightarrow \text{HCl} + \text{HCHO} + \text{OH}$	2	5.9×10^{-11}		Atkinson et al. (2006)
Cl59	$\text{Cl} + \text{ACO}_2 \longrightarrow \text{HCl} + \text{HO}_2$	2	1.9×10^{-13}		Atkinson et al. (2006)
Cl60	$\text{Cl} + \text{ACTA} \longrightarrow \text{HCl} + \text{MO}_2$	2	2.65×10^{-14}		Atkinson et al. (2006)
Cl61	$\text{Cl} + \text{PAN} \longrightarrow \text{HCl} + \text{HCHO} + \text{CO} + \text{NO}_2$	2	2.0×10^{-14}		Atkinson et al. (2006)
Cl62	$\text{Cl} + \text{MO}_2 \longrightarrow 0.5 \text{ ClO} + 0.5 \text{ HCHO} + 0.5 \text{ HO}_2$	2	1.6×10^{-10}		Sander et al. (2006)
Cl63	$\text{HO}_2 + 0.5 \text{ HCl} + 0.5 \text{ CO} + 0.5 \text{ H}_2\text{O}$	2	3.3×10^{-12}	-115	Sander et al. (2006)
Cl64	$\text{ClO} + \text{MO}_2 \longrightarrow \text{Cl} + \text{HCHO} + \text{HO}_2$	2	$7.78 \times 10^{-18} \times (T)^2$	-152	MCM *
Cl65	$\text{RCI} + \text{OH} \longrightarrow \text{ClRO}_2 + \text{H}_2\text{O}$	2	4.06×10^{-12}	360	Toyota et al. (2004)
Cl66	$\text{ClRO}_2 + \text{NO} \longrightarrow \text{HCl} + \text{MCO}_3 + \text{NO}_2$	2	7.50×10^{-12}		Toyota et al. (2004)
Cl67	$\text{ClRO}_2 + \text{HO}_2 \longrightarrow \text{XOR} + \text{H}_2\text{O}$	2	1.10×10^{-13}	1020	Toyota et al. (2004)
Cl68	$\text{ClRO}_2 + \text{ClRO}_2 \longrightarrow 2 \text{ HCl} + 2 \text{ MCO}_3$	2	1.76×10^{-12}		Toyota et al. (2004)
	$\text{ClRO}_2 + \text{MO}_2 \longrightarrow \text{HCl} + \text{MCO}_3 + \text{HO}_2 + \text{HCHO}$	2			
Br01	$\text{Br} + \text{O}_3 \longrightarrow \text{BrO} + \text{O}_2$	2	1.7×10^{-11}	-800	Atkinson et al. (2006)
Br02	$\text{Br} + \text{HO}_2 \longrightarrow \text{HBr} + \text{O}_2$	2	7.7×10^{-12}	-450	Atkinson et al. (2006)
Br03	$\text{Br} + \text{H}_2\text{O}_2 \longrightarrow 0.5 \text{ HBr} + 0.5 \text{ HO}_2 + 0.5 \text{ HOBr} + 0.5 \text{ OH}$	2	5.0×10^{-16}		Atkinson et al. (2006)
Br04	$\text{Br} + \text{NO}_2 + \text{M} \longrightarrow \text{BrNO}_2$	3	†		Atkinson et al. (2006)
Br05	$\text{Br} + \text{NO}_3 \longrightarrow \text{BrO} + \text{NO}_2$	2	1.6×10^{-11}		Atkinson et al. (2006)
Br06	$\text{Br}_2 + \text{OH} \longrightarrow \text{HOBr} + \text{Br}$	2	1.9×10^{-11}	240	Atkinson et al. (2006)
Br07	$\text{Br}_2 + \text{O}^3\text{P} \longrightarrow \text{BrO} + \text{Br}$	2	5.12×10^{-13}	989	Harwood et al., 1998
Br08	$\text{Br}_2 + \text{hv} \longrightarrow 2 \text{ Br}$	1	§		
Br10	$\text{BrO} + \text{O}^3\text{P} \longrightarrow \text{Br} + \text{O}_2$	2	1.9×10^{-11}	230	Atkinson et al. (2006)
Br11	$\text{BrO} + \text{OH} \longrightarrow \text{Br} + \text{HO}_2$	2	1.8×10^{-11}	250	Atkinson et al. (2006)
Br12	$\text{BrO} + \text{HO}_2 \longrightarrow \text{HOBr} + \text{O}_2$	2	4.5×10^{-12}	500	Atkinson et al. (2006)
Br13	$\text{BrO} + \text{NO} \longrightarrow \text{Br} + \text{NO}_2$	2	8.7×10^{-12}	260	Atkinson et al. (2006)
Br14	$\text{BrO} + \text{NO}_2 + \text{M} \longrightarrow \text{BrNO}_3$	3	†		Sander et al. (2006)
Br15	$\text{BrO} + \text{NO}_3 \longrightarrow \text{Br} + \text{NO}_2 + \text{O}_2$	2	1.0×10^{-12}		Atkinson et al. (2006)

Table S3: continued.

no	reaction	n	$A [(\text{cm}^{-3})^{1-n} \text{s}^{-1}]$	$-E_a / R [\text{K}]$	reference
Br16	$\text{BrO} + \text{O}_3 \longrightarrow \text{Br} + 2 \text{O}_2$	2	1.0×10^{-12}	-3200	Sander et al. (2006)
Br17	$\text{BrO} + \text{BrO} \longrightarrow 2 \text{Br} + \text{O}_2$	2	2.7×10^{-12}		Atkinson et al. (2006)
Br18	$\text{BrO} + \text{BrO} \longrightarrow \text{Br}_2 + \text{O}_2$	2	2.9×10^{-14}	840	Atkinson et al. (2006)
Br19	$\text{BrO} + \text{O}_2 + \text{h}\nu \longrightarrow \text{Br} + \text{O}_3$	1	\S		
Br21	$\text{HBr} + \text{OH} \longrightarrow \text{Br} + \text{H}_2\text{O}$	2	6.7×10^{-12}	155	Atkinson et al. (2006)
Br22	$\text{HBr} + \text{NO}_3 \longrightarrow \text{Br} + \text{HNO}_3$	2	1.0×10^{-16}		Atkinson et al. (2006)
Br23	$\text{HOBr} + \text{O}^3\text{P} \longrightarrow \text{OH} + \text{BrO}$	2	1.2×10^{-10}	-430	Atkinson et al. (2006)
Br24	$\text{HOBr} + \text{h}\nu \longrightarrow \text{Br} + \text{OH}$	1	\S		
Br25	$\text{BrNO}_2 + \text{h}\nu \longrightarrow \text{Br} + \text{NO}_2$	1	\S		
Br26	$\text{BrNO}_3 + \text{O}^3\text{P} \longrightarrow \text{Br} + \text{NO}_3$	2	1.9×10^{-11}	215	Atkinson et al. (2006)
Br27	$\text{BrNO}_3 + \text{Br} \longrightarrow \text{Br}_2 + \text{NO}_3$	2	2.08×10^{-11}	320	Orlando and Tyndall (1996)
Br28	$\text{BrNO}_3 + \text{M} \longrightarrow \text{BrO} + \text{NO}_2$	2	\dagger		Orlando and Tyndall (1996)
Br29	$\text{BrNO}_3 + \text{h}\nu \longrightarrow \text{Br} + \text{NO}_3$	1	\S		
Br30	$\text{Br} + \text{ETHE} + \text{O}_2 \longrightarrow \text{HBr} + \text{BrRO}_2$	2	1.3×10^{-13}		Atkinson et al. (2006)
Br31	$\text{Br} + \text{HCHO} \longrightarrow \text{HBr} + \text{CO} + \text{HO}_2$	2	7.7×10^{-12}	-580	Atkinson et al. (2006)
Br32	$\text{Br} + \text{ALD2} \longrightarrow \text{HBr} + \text{MCO}_3$	2	1.8×10^{-11}	-460	Atkinson et al. (2006)
Br33	$\text{Br} + \text{ROOH} \longrightarrow \text{MO}_2 + \text{HBr}$	2	2.66×10^{-12}	-1610	Kondo and Benson (1984)
Br34	$\text{Br} + \text{MO}_2 \longrightarrow \text{HBr} + \text{CHO}_2$	2	4.4×10^{-13}		Francisco and Crowley (2006)
Br35	$\text{BrO} + \text{HCHO} + \text{O}_2 \longrightarrow \text{HOBr} + \text{CO} + \text{HO}_2$	2	1.5×10^{-14}		Hansen et al. (1999)
Br36	$\text{BrO} + \text{MO}_2 \longrightarrow \text{Br} + \text{HCHO} + \text{HO}_2 + \text{O}_2$	2	$4.1 \times 10^{-13} \times 0.25$	800	Atkinson et al. (2006)
Br37	$\text{BrO} + \text{MO}_2 \longrightarrow \text{HOBr} + \text{HCHO}$	2	$4.1 \times 10^{-13} \times 0.75$	800	Atkinson et al. (2006)
Br38	$\text{RBr} + \text{OH} \longrightarrow \text{BrRO}_2 + \text{H}_2\text{O}$	2	$1.03 \times 10^{-17} \times (T)^2$	-422	MCM *
Br39	$\text{BrRO}_2 + \text{NO} \longrightarrow \text{Br} + \text{ALD2} + \text{NO}_2$	2	4.06×10^{-12}	360	Toyota et al. (2004)
Br40	$\text{BrRO}_2 + \text{HO}_2 \longrightarrow \text{XOR} + \text{H}_2\text{O}$	2	7.50×10^{-12}		Toyota et al. (2004)
Br41	$\text{BrRO}_2 + \text{BrRO}_2 \longrightarrow 2 \text{Br} + 2 \text{ALD2}$	2	6.15×10^{-14}		Toyota et al. (2004)
Br42	$\text{BrRO}_2 + \text{MO}_2 \longrightarrow \text{Br} + \text{ALD2} + \text{HO}_2 + \text{HCHO}$	2	2.45×10^{-12}	1247	Toyota et al. (2004)

Table S3: continued.

no	reaction	n	$A [(\text{cm}^{-3})^{1-n} \text{s}^{-1}]$	$-E_a / R [\text{K}]$	reference
I01	$\text{I} + \text{O}_3 \longrightarrow \text{IO} + \text{O}_2$	2	2.1×10^{-11}	-830	Atkinson et al. (2006)
I02	$\text{I} + \text{HO}_2 \longrightarrow \text{HI} + \text{O}_2$	2	1.5×10^{-11}	-1090	Atkinson et al. (2006)
I03	$\text{I} + \text{NO} + \text{M} \longrightarrow \text{INO}$	3	†		Atkinson et al. (2006)
I04	$\text{I} + \text{NO}_2 + \text{M} \longrightarrow \text{INO}_2$	3	†		Atkinson et al. (2006)
I06	$\text{I} + \text{I} \longrightarrow \text{I}_2$	2	$1.0 \times 10^{-32} \times [\text{N}_2] + 1.9 \times 10^{-32} \times [\text{O}_2]$		Jenkin et al. (1990)
I07	$\text{I} + \text{IO} \longrightarrow \text{I}_2\text{O}$	2	1.7×10^{-10}		Bloss et al. (2001)
I08	$\text{I} + \text{I}_2\text{O} \longrightarrow \text{IO} + \text{I}_2$	2	2.1×10^{-10}		Bloss et al. (2001)
I09	$\text{I}_2 + \text{O}^3\text{P} \longrightarrow \text{IO} + \text{I}$	2	1.25×10^{-10}		Atkinson et al. (2006)
I10	$\text{I}_2 + \text{OH} \longrightarrow \text{HOI} + \text{I}$	2	2.1×10^{-10}		Atkinson et al. (2006)
I11	$\text{I}_2 + \text{NO}_3 \longrightarrow \text{I} + \text{INO}_3$	2	1.5×10^{-12}		Atkinson et al. (2006)
I12	$\text{I}_2 + \text{h}\nu \longrightarrow 2\text{I}$	1	§		
I13	$\text{HI} + \text{OH} \longrightarrow \text{I} + \text{H}_2\text{O}$	2	1.6×10^{-11}	440	Atkinson et al. (2006)
I15	$\text{HOI} + \text{h}\nu \longrightarrow \text{I} + \text{OH}$	1	§		
I16	$\text{HOI} + \text{OH} \longrightarrow \text{IO} + \text{H}_2\text{O}$	2	5.0×10^{-12}		Riffault et al. (2005)
I17	$\text{IO} + \text{O}^3\text{P} \longrightarrow \text{I} + \text{O}_2$	2	1.4×10^{-10}		Atkinson et al. (2006)
I18	$\text{IO} + \text{HO}_2 \longrightarrow \text{HOI} + \text{O}_2$	2	1.4×10^{-11}	540	Atkinson et al. (2006)
I19	$\text{IO} + \text{NO} \longrightarrow \text{I} + \text{NO}_2$	2	7.15×10^{-12}	300	Atkinson et al. (2006)
I20	$\text{IO} + \text{NO}_2 + \text{M} \longrightarrow \text{INO}_3$	3	†		Atkinson et al. (2006)
I23	$\text{IO} + \text{O}_2 + \text{h}\nu \longrightarrow \text{I} + \text{O}_3$	1	§		
I24	$\text{IO} + \text{OIO} + \text{M} \longrightarrow \text{I}_2\text{O}_3$	2	1.0×10^{-10}		Gómez-Martín et al. (2007)
I25	$\text{IO} + \text{IO} \longrightarrow 0.4 \text{I} + 0.4 \text{OIO} + 0.6 \text{IO}_2$	2	5.4×10^{-11}	180	Bloss et al. (2001)
I26	$\text{OIO} + \text{OH} \longrightarrow \text{HIO}_3$	2	2.2×10^{-10}	243	Plane et al. (2006)
I27	$\text{OIO} + \text{NO} \longrightarrow \text{NO}_2 + \text{IO}$	2	1.1×10^{-12}	542	Atkinson et al. (2006)
I28	$\text{OIO} + \text{h}\nu \longrightarrow \text{I} + \text{O}_2$	1	§		
I29	$\text{OIO} + \text{OIO} \longrightarrow \text{I}_2\text{O}_4$	2	1.5×10^{-10}		Gómez-Martín et al. (2007)
I30a	$\text{I}_2\text{O}_2 \longrightarrow \text{IO} + \text{IO}$	1	4.0×10^{-2}		Kaltsayannis and Plane (2008)
I30b	$\text{I}_2\text{O}_2 \longrightarrow \text{OIO} + \text{I}$	1	$1.0 \times 10^{+1}$		Kaltsayannis and Plane (2008)

Table S3: continued.

no	reaction	n	$A [(\text{cm}^{-3})^{1-n} \text{s}^{-1}]$	$-E_a / R [\text{K}]$	reference
I31	$\text{I}_2\text{O}_2 + \text{h}\nu \rightarrow \text{IO} + \text{IO}$	1	§		Saunders and Plane (2005)
I32	$\text{I}_2\text{O}_2 + \text{O}_3 \rightarrow \text{I}_2\text{O}_3 + \text{O}_2$	2	1.0×10^{-12}	-2620	Atkinson et al. (2006)
I38	$\text{INO} + \text{INO} \rightarrow \text{I}_2 + 2 \text{NO}$	2	8.4×10^{-11}		van den Bergh and Troe (1976)
I39	$\text{INO} \rightarrow \text{I} + \text{NO}$	1	†		Atkinson et al. (2006)
I40	$\text{INO}_2 + \text{INO}_2 \rightarrow \text{I}_2 + 2 \text{NO}_2$	2	4.7×10^{-13}	-1670	van den Bergh and Troe (1976)
I41	$\text{INO}_2 \rightarrow \text{I} + \text{NO}_2$	1	†		
I42	$\text{INO}_2 + \text{h}\nu \rightarrow \text{I} + \text{NO}_2$	1	§		Kaltsayannis and Plane (2008)
I43	$\text{INO}_3 \rightarrow \text{IO} + \text{NO}_2$	1	2.1×10^{15}	-13670	
I44	$\text{INO}_3 + \text{h}\nu \rightarrow \text{I} + \text{NO}_3$	1	§		Kaltsayannis and Plane (2008)
I45	$\text{INO}_3 + \text{I} \rightarrow \text{I}_2 + \text{NO}_3$	2	9.1×10^{-11}	-146	
I46	$\text{CH}_2\text{I}_2 + \text{O}_2 + \text{h}\nu \rightarrow \text{I} + \text{IO} + \text{HCHO}$	1	§		Atkinson et al. (2006)
I47	$\text{CH}_3\text{I} + \text{OH} \rightarrow 0.7 \text{H}_2\text{O} + 0.7 \text{IRO}_2 + 0.3 \text{CH}_3\text{OH} + 0.3 \text{I}$	2	4.3×10^{-12}	-1120	
I48	$\text{CH}_3\text{I} + \text{h}\nu \rightarrow \text{I} + \text{MO}_2$	1	§		Cotter et al. (2003)
I49	$\text{C}_2\text{H}_5\text{I} + \text{OH} + \text{O}_2 \rightarrow 0.5 \text{H}_2\text{O} + 0.5 \text{IRO}_2 + 0.5 \text{C}_2\text{H}_5\text{OH} + 0.5 \text{I}$	2	7.7×10^{-13}		
I50	$\text{C}_2\text{H}_5\text{I} + \text{h}\nu \rightarrow \text{I} + \text{ETO}_2$	1	§		Cotter et al. (2003)
I51	$\text{C}_3\text{H}_7\text{I} + \text{OH} + \text{O}_2 \rightarrow 0.7 \text{H}_2\text{O} + 0.7 \text{IRO}_2 + 0.3 \text{C}_2\text{H}_5\text{OH} + 0.3 \text{I}$	2	2.05×10^{-12}		
I52	$\text{C}_3\text{H}_7\text{I} + \text{h}\nu \rightarrow \text{I} + \text{ETO}_2$	1	§		
I53	$\text{IO} + \text{MO}_2 + \text{O}_2 \rightarrow \text{HCHO} + \text{HO}_2 + \text{I}$	2	2.0×10^{-12}		Dillon et al. (2006)
I54	$\text{IRO}_2 + \text{NO} \rightarrow \text{I} + \text{HCHO} + \text{NO}_2$	2	4.06×10^{-12}	360	Toyota et al. (2004)
I55	$\text{IRO}_2 + \text{HO}_2 \rightarrow \text{XOR} + \text{H}_2\text{O}$	2	7.50×10^{-12}		Toyota et al. (2004)
I56	$\text{IRO}_2 + \text{IRO}_2 \rightarrow 2 \text{I} + 2 \text{HCHO}$	2	6.15×10^{-14}	1247	Toyota et al. (2004)
I57	$\text{IRO}_2 + \text{MO}_2 \rightarrow \text{I} + \text{HCHO} + \text{HO}_2 + \text{HCHO}$	2	2.45×10^{-12}		Toyota et al. (2004)

Table S3: continued.

no	reaction	n	$A [(\text{cm}^{-3})^{1-n} \text{s}^{-1}]$	$-E_a / R [\text{K}]$	reference
Hx01	$\text{Cl} + \text{BrCl} \longrightarrow \text{Br} + \text{Cl}_2$	2	1.45×10^{-11}	-135	Clyne and Cruse (1972)
Hx02	$\text{Cl} + \text{Br}_2 \longrightarrow \text{BrCl} + \text{Br}$	2	2.3×10^{-10}		Bedjanian et al. (1998c)
Hx03	$\text{Cl} + \text{I}_2 \longrightarrow \text{I} + \text{ICl}$	2	2.7×10^{-10}		Bedjanian et al. (1996)
Hx04	$\text{Cl} + \text{IO} \longrightarrow \text{I} + \text{ClO}$	2	4.4×10^{-11}		Bedjanian et al. (1996)
Hx05	$\text{Br} + \text{OClO} \longrightarrow \text{BrO} + \text{ClO}$	2	2.7×10^{-11}	-1300	Atkinson et al. (2006)
Hx06	$\text{Br} + \text{Cl}_2 \longrightarrow \text{BrCl} + \text{Cl}$	2	1.1×10^{-15}	170	Dolson and Leone (1987)
Hx07	$\text{Br} + \text{Cl}_2\text{O}_2 \longrightarrow \text{BrCl} + \text{Cl} + \text{O}_2$	2	5.9×10^{-12}		Atkinson et al. (2006)
Hx08	$\text{Br} + \text{BrCl} \longrightarrow \text{Br}_2 + \text{Cl}$	2	3.32×10^{-15}		Baulch et al. (1981)
Hx09	$\text{Br} + \text{I}_2 \longrightarrow \text{I} + \text{IBr}$	2	1.2×10^{-10}		Bedjanian et al. (1997)
Hx10	$\text{Br} + \text{IO} \longrightarrow \text{I} + \text{BrO}$	2	2.7×10^{-11}		Bedjanian et al. (1998b)
Hx11	$\text{Br} + \text{IBr} \longrightarrow \text{I} + \text{Br}_2$	2	2.7×10^{-11}		Bedjanian et al. (1998a)
Hx12	$\text{I} + \text{Br}_2 \longrightarrow \text{Br} + \text{IBr}$	2	1.65×10^{-13}		Bedjanian et al. (1998a)
Hx13	$\text{I} + \text{BrO} \longrightarrow \text{IO} + \text{Br}$	2	1.2×10^{-11}		Sander et al. (2006)
Hx14	$\text{I}_2 + \text{BrO} \longrightarrow \text{IO} + \text{IBr}$	2	2.0×10^{-14}	430	Bedjanian et al. (1998b)
Hx15	$\text{BrO} + \text{ClO} \longrightarrow \text{Br} + \text{OClO}$	2	1.6×10^{-12}	220	Atkinson et al. (2006)
Hx16	$\text{BrO} + \text{ClO} \longrightarrow \text{Br} + \text{Cl} + \text{O}_2$	2	2.9×10^{-12}	170	Atkinson et al. (2006)
Hx17	$\text{BrO} + \text{ClO} \longrightarrow \text{BrCl} + \text{O}_2$	2	5.8×10^{-13}		Atkinson et al. (2006)
Hx18	$\text{BrO} + \text{IBr} \longrightarrow \text{Br}_2 + \text{IO}$	2	2.5×10^{-14}		Bedjanian et al. (1998b)
Hx19	$\text{IO} + \text{ClO} \longrightarrow \text{ICl} + \text{O}_2$	2	$4.7 \times 10^{-12} \times 0.2$	280	Atkinson et al. (2006)
Hx20	$\text{IO} + \text{ClO} \longrightarrow \text{I} + \text{Cl} + \text{O}_2$	2	$4.7 \times 10^{-12} \times 0.25$	280	Atkinson et al. (2006)
Hx21	$\text{IO} + \text{ClO} \longrightarrow \text{I} + \text{OClO}$	2	$4.7 \times 10^{-12} \times 0.55$	280	Atkinson et al. (2006)
Hx22	$\text{IO} + \text{BrO} \longrightarrow \text{Br} + \text{I} + \text{O}_2$	2	$1.5 \times 10^{-11} \times 0.2$	510	Atkinson et al. (2006)
Hx23	$\text{IO} + \text{BrO} \longrightarrow \text{Br} + \text{OIO}$	2	$1.5 \times 10^{-11} \times 0.8$	510	Atkinson et al. (2006)
Hx24	$\text{IBr} + \text{OH} \longrightarrow 0.85 \text{ HOI} + 0.85 \text{ Br} + 0.15 \text{ HOBr} + 0.15 \text{ I}$	2	1.4×10^{-10}		Riffault et al. (2005)
Hx25	$\text{IBr} + \text{h}\nu \longrightarrow \text{I} + \text{Br}$	1	\S		Clyne and Cruse (1972)
Hx26	$\text{ICl} + \text{Br} \longrightarrow \text{BrCl} + \text{I}$	2	3.01×10^{-14}		Chesnokov (1991)
Hx27	$\text{ICl} + \text{Cl} \longrightarrow \text{Cl}_2 + \text{I}$	2	1.20×10^{-11}		Loewenstein and Anderson (1985)
Hx28	$\text{ICl} + \text{OH} \longrightarrow \text{HOCl} + \text{I}$	2	2.01×10^{-11}		

Table S3: continued.

no	reaction	n	$A [(\text{cm}^{-3})^{1-n} \text{s}^{-1}]$	$-E_a / R [\text{K}]$	reference
Hx29	$\text{ICl} + \text{h}\nu \longrightarrow \text{I} + \text{Cl}$	1	§		Clyne et al. (1976)
Hx30	$\text{BrCl} + \text{O}^3\text{P} \longrightarrow \text{BrO} + \text{Cl}$	2	2.09×10^{-11}		Kukui et al. (1996)
Hx31	$\text{BrCl} + \text{OH} \longrightarrow \text{HOBr} + \text{Cl}$	2	1.5×10^{-12}		
Hx32	$\text{BrCl} + \text{h}\nu \longrightarrow \text{Br} + \text{Cl}$	1	§		Sander et al. (2006)
Hx33	$\text{Cl} + \text{CH}_3\text{I} + \text{O}_2 \longrightarrow 0.7 \text{HCl} + 0.7 \text{IRO}_2 + 0.3 \text{RCI} + 0.3 \text{I}$	2	2.9×10^{-11}	-1000	
Hx34	$\text{Cl} + \text{C}_2\text{H}_5\text{I} + \text{O}_2 \longrightarrow 0.5 \text{HCl} + 0.5 \text{IRO}_2 + 0.5 \text{RCI} + 0.5 \text{I}$	2	1.6×10^{-11}		Cotter et al. (2001)
Hx35	$\text{Cl} + \text{C}_3\text{H}_7\text{I} + \text{O}_2 \longrightarrow 0.7 \text{HCl} + 0.7 \text{IRO}_2 + 0.3 \text{RCI} + 0.3 \text{I}$	2	5.67×10^{-11}		Cotter et al. (2001)
Hx36	$\text{CH}_2\text{BrI} + \text{h}\nu \longrightarrow \text{I} + \text{Br} + 2 \text{HO}_2 + \text{CO}$	1	§		
Hx38	$\text{CH}_2\text{ClI} + \text{h}\nu \longrightarrow \text{I} + \text{Cl} + 2 \text{HO}_2 + \text{CO}$	1	§		

Notes:

n is the order of the reaction; the rate coefficients are calculated with the standard Arrhenius expression: $k = A \times e^{(-E_a/RT)}$.

† rate coefficients for pressure-dependent combination and dissociation reactions calculated using the Lindemann-Hinshelwood expression (Atkinson et al., 2006).

‡ special rate functions (see corresponding reference).

§ photolysis rates calculated by MISTRA using cross-sections and quantum yields from Sander et al. (2006).

* rate coefficients taken from the Master Chemical Mechanism v3.1 (<http://mcm.leeds.ac.uk/MCMv3.1/>).

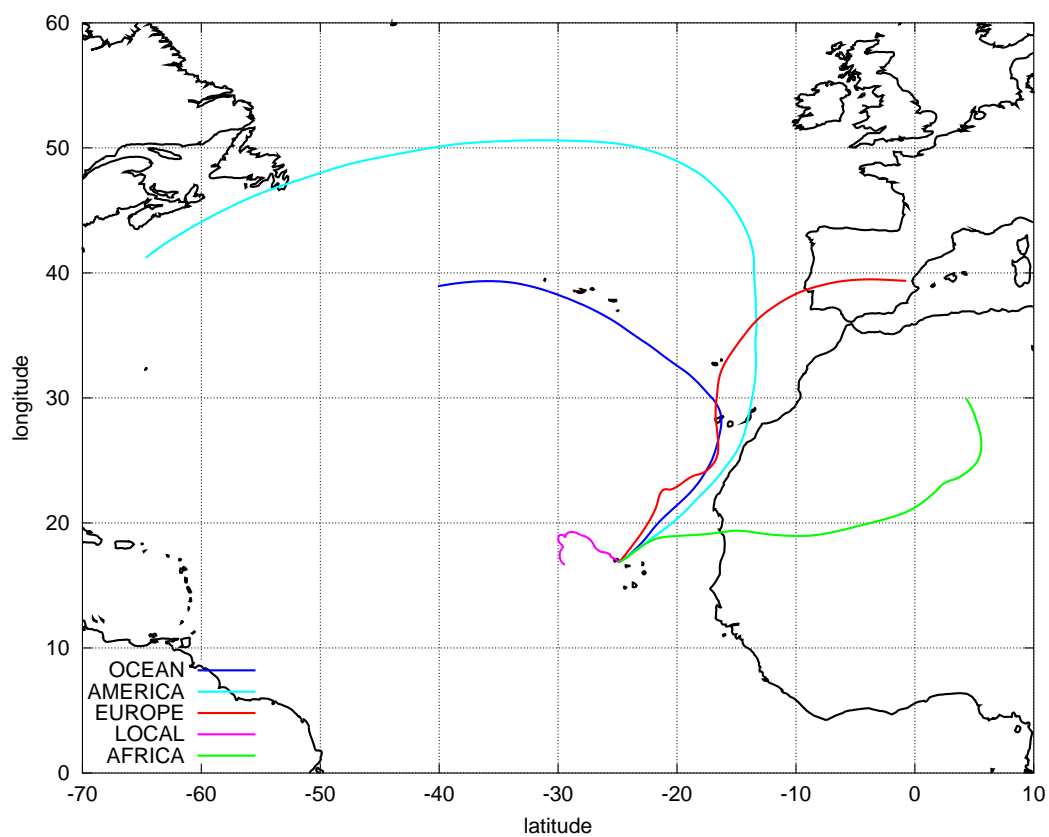


Figure S1: Map of the Atlantic Ocean with the position of the Cape Verde Atmospheric Observatory (CVAO) and typical air mass back-trajectories representative of each model scenario.

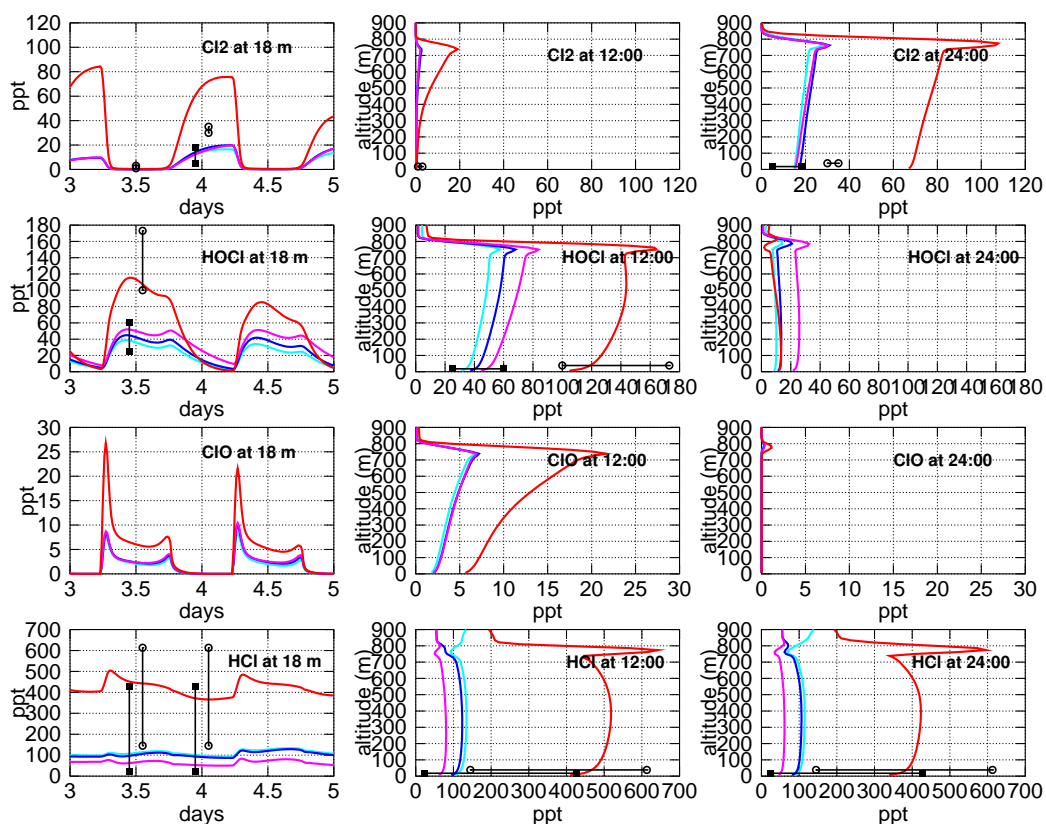


Figure S2: Modelled time series and vertical profiles of Cl_2 , HOCl, ClO, HCl in the BASE model scenarios (OCEAN in blue, AMERICA in cyan, EUROPE in red, LOCAL in magenta). The ranges of published observations are shown in black for clean (squares) and semi-polluted (circles) conditions. Time in days since model start.

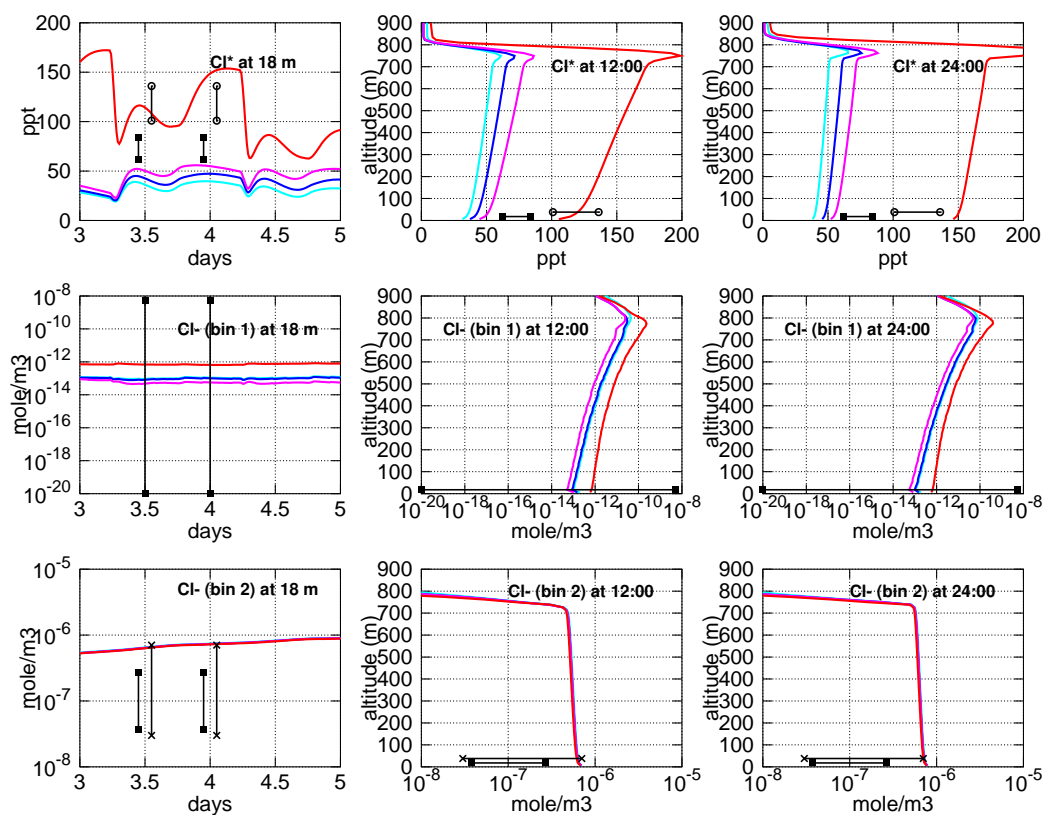


Figure S3: Modelled time series and vertical profiles of Cl^* (gas-phase) and Cl^- (bin 1 = sulphate aerosol; bin 2 = sea-salt) in the BASE model scenarios (OCEAN in blue, AMERICA in cyan, EUROPE in red, LOCAL in magenta). The ranges of published observations are shown in black for clean (squares) and semi-polluted (circles) conditions. The bulk aerosol measurements by Keene et al. (2009) are shown as asterisks. Time in days since model start.

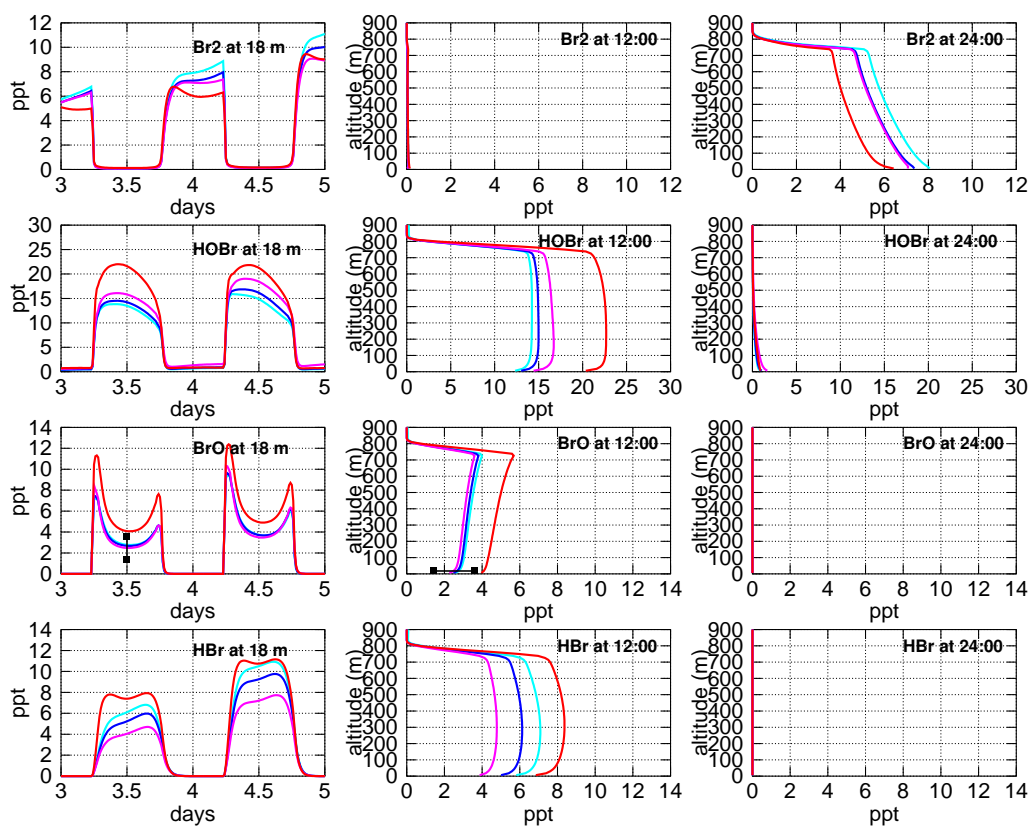


Figure S4: Modelled time series and vertical profiles of Br_2 , HOBr, BrO, HBr in the BASE model scenarios (OCEAN in blue, AMERICA in cyan, EUROPE in red, LOCAL in magenta). The ranges of available observations are shown as black squares. Time in days since model start.

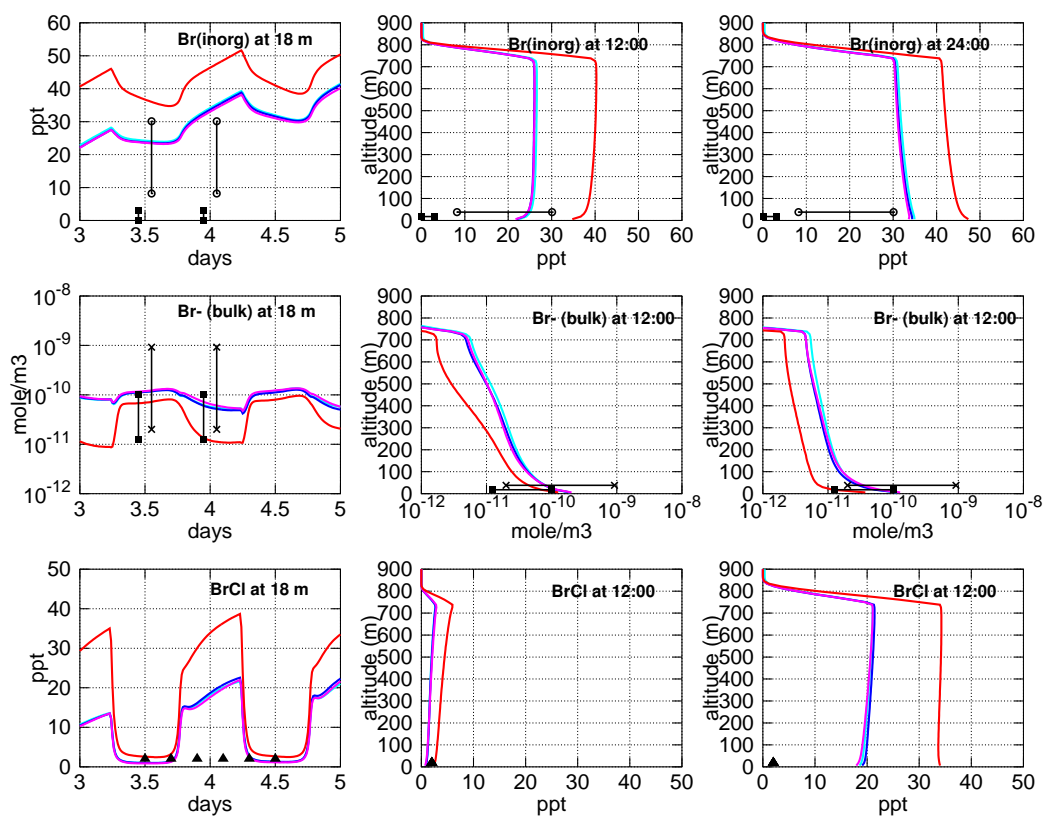


Figure S5: Modelled time series and vertical profiles of Br^- (bulk aerosol) and Br_{inorg} , BrCl (gas-phase) in the BASE model scenarios (OCEAN in blue, AMERICA in cyan, EUROPE in red, LOCAL in magenta). The ranges of published observations are shown in black for clean (squares) and semi-polluted (circles) conditions. The bulk aerosol measurements by Keene et al. (2009) are shown as asterisks. The detection limit of BrCl is shown as black triangles. Time in days since model start.

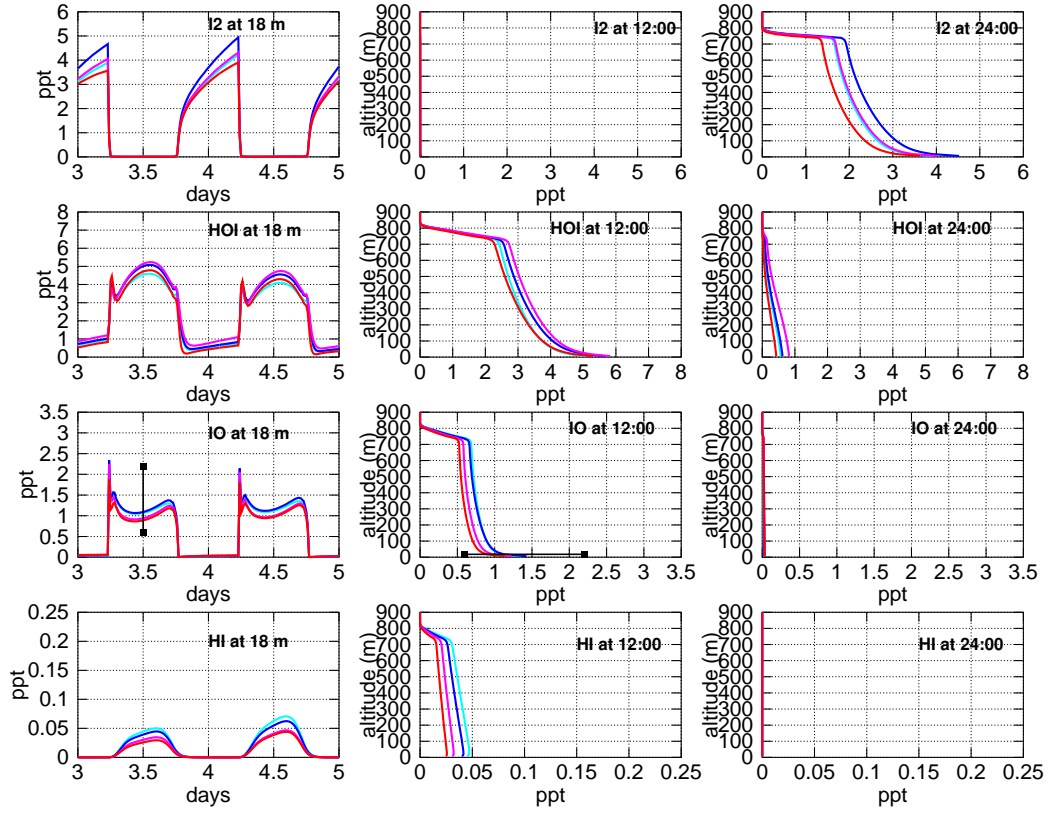


Figure S6: Modelled time series and vertical profiles of I_2 , HOI, IO, HI in the IOD model scenarios (OCEAN in blue, AMERICA in cyan, EUROPE in red, LOCAL in magenta). The ranges of available observations are shown as black squares. Time in days since model start.

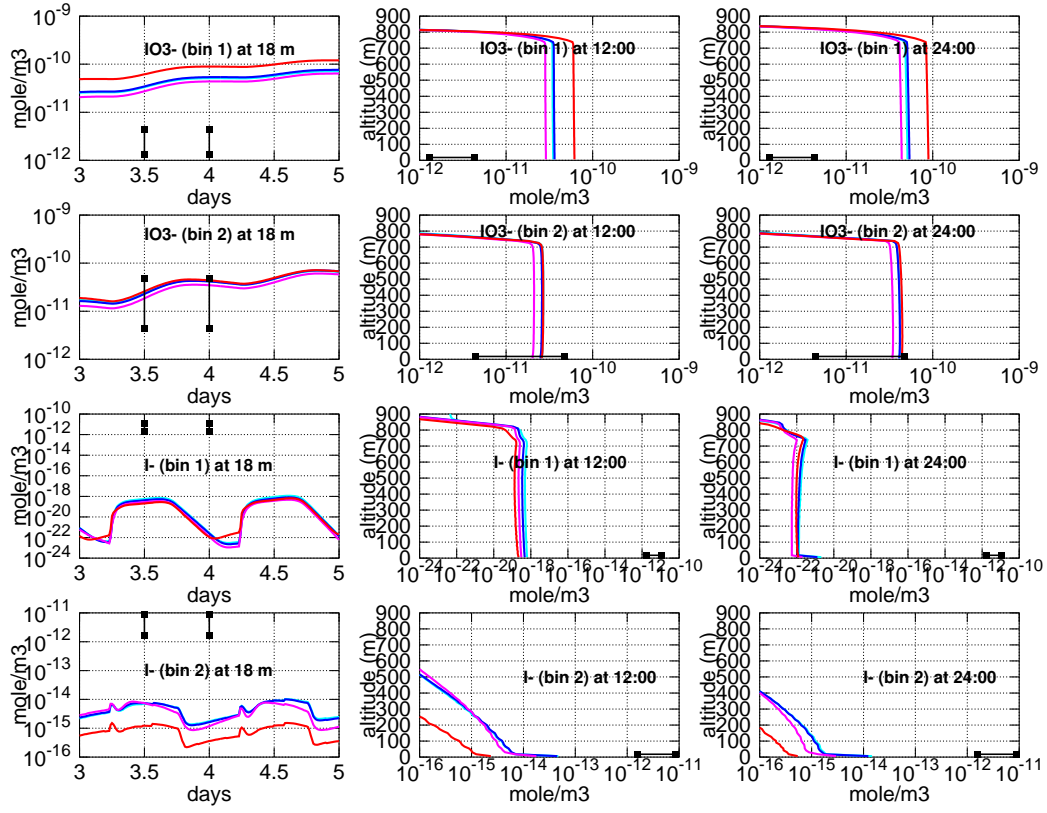


Figure S7: Modelled time series and vertical profiles of IO_3^- , I^- (bin 1 = sulphate aerosol; bin 2 = sea-salt), in the IOD model scenarios (OCEAN in blue, AMERICA in cyan, EUROPE in red, LOCAL in magenta). The ranges of available observations are shown as black squares. Time in days since model start.

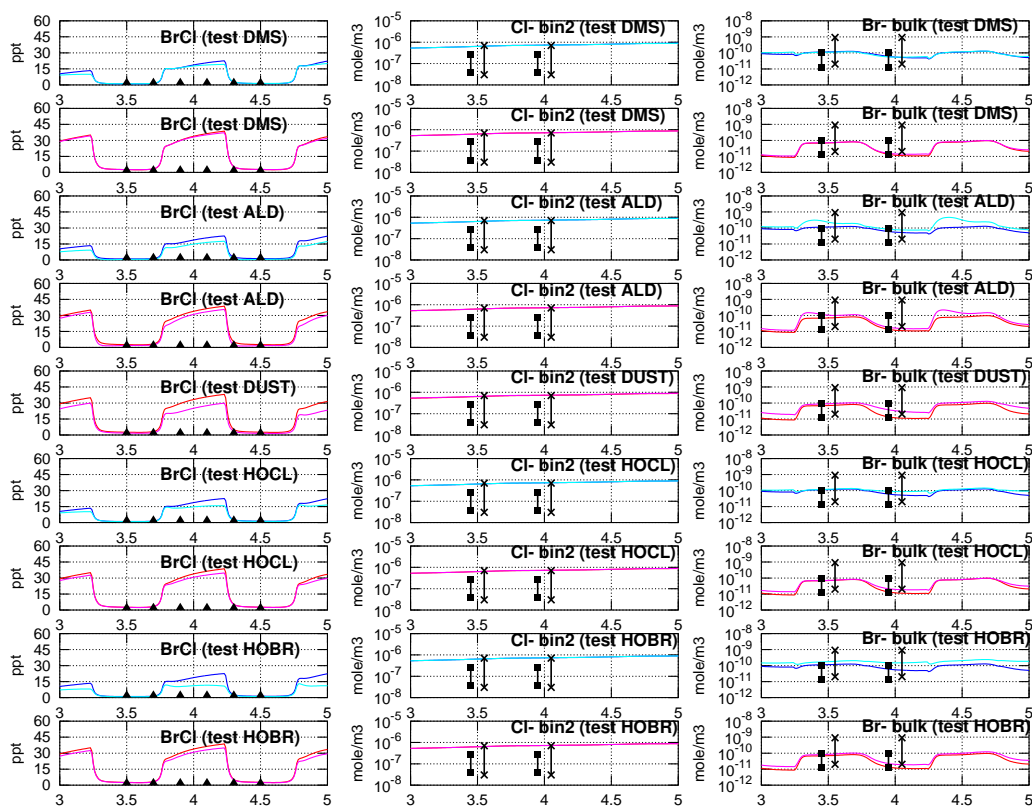


Figure S8: Modelled time series at 18 m of BrCl (gas-phase), Cl^- (bin 2 = sea-salt), Br^- (bulk aerosol) in the BASE and test (DMS, ALD, DUST, HOCL, HOBR) cases. (BASE case OCEAN scenario in blue, test case OCEAN scenario in cyan, BASE case EUROPE scenario in red, test case EUROPE scenario in magenta). The ranges of published observations are shown in black for clean (squares) and semi-polluted (circles) conditions. The bulk aerosol measurements by Keene et al. (2009) are shown as asterisks. The detection limit of BrCl is shown as black triangles. Time in days since model start.

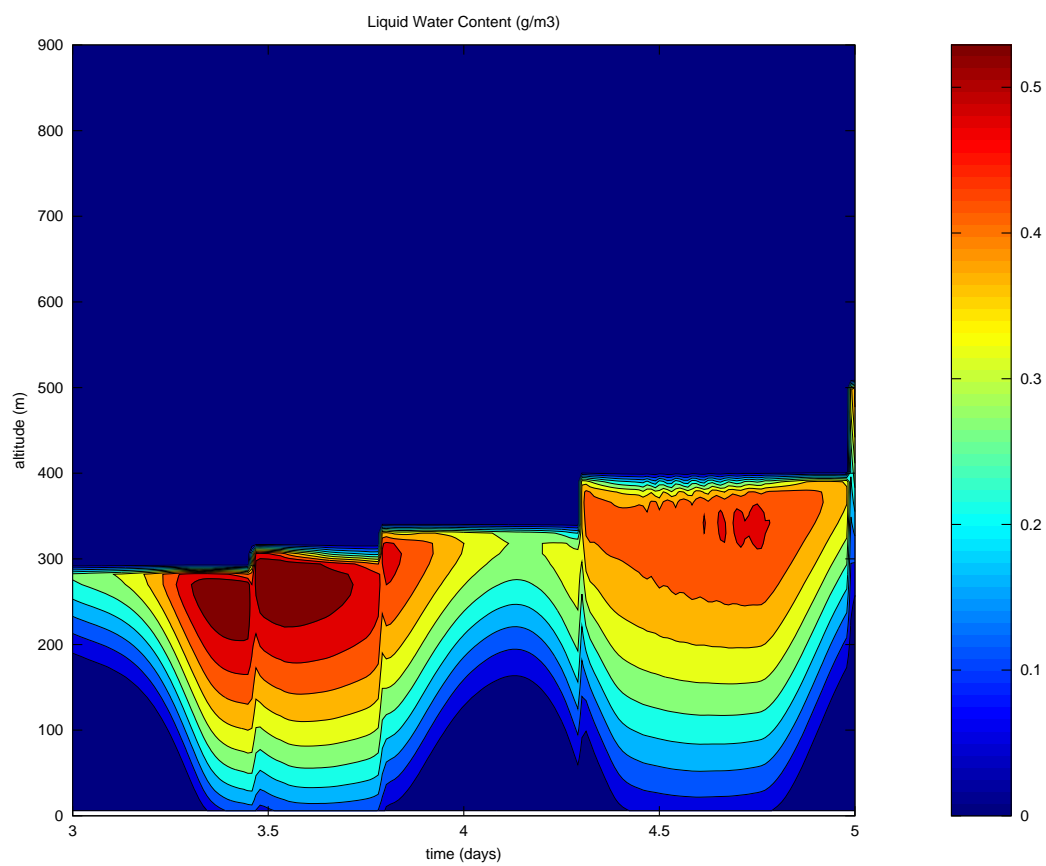


Figure S9: Formation of clouds in the AFRICA scenario (BASE case). Time in days since model start.

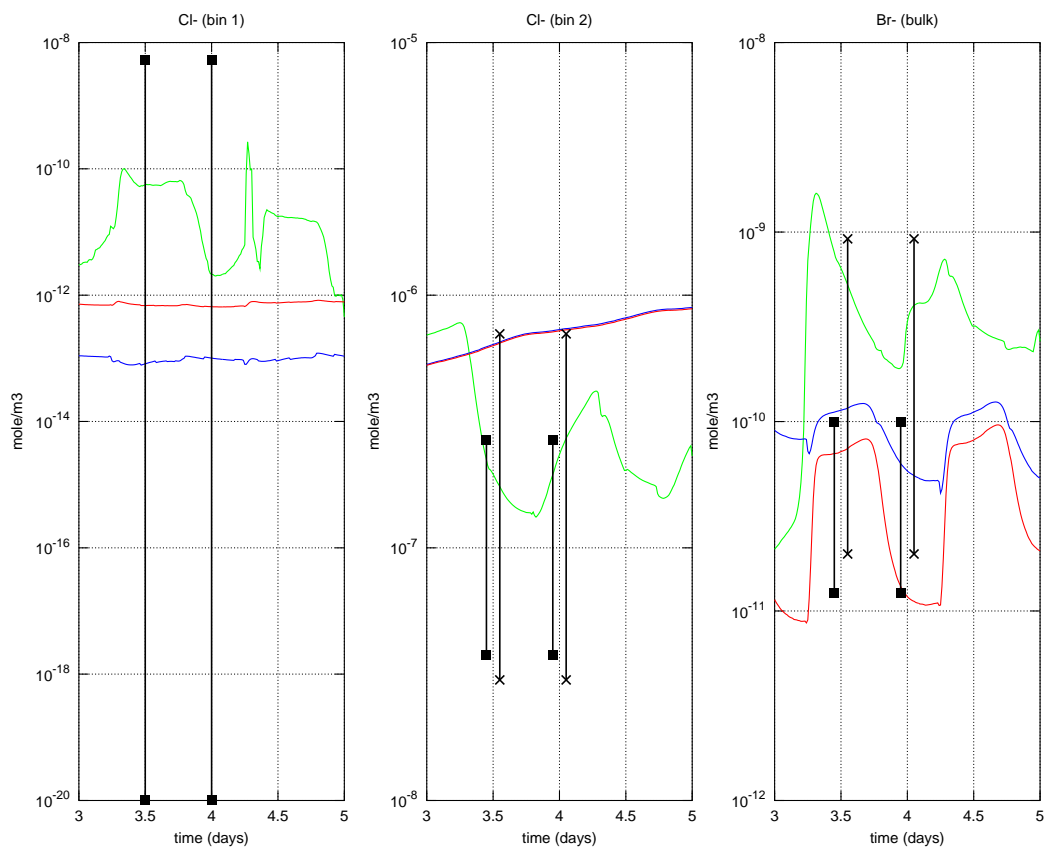


Figure S10: Modelled time series (at 18 m) of Cl^- (bin 1 = sulphate aerosol; bin 2 = sea-salt) and Br^- (bulk aerosol) in the BASE case (OCEAN in blue, EUROPE in red, AFRICA in green). The ranges of published observations are shown as black squares. The bulk aerosol measurements by Keene et al. (2009) are shown as asterisks. Time in days since model start.

References

- J. D. Allan, D. O. Topping, N. Good, M. Irwin, M. Flynn, P. I. Williams, H. Coe, A. R. Baker, M. Martino, N. Niedermeier, A. Wiedensohler, S. Lehmann, K. Müller, H. Herrmann, and G. McFiggans. Composition and properties of atmospheric particles in the eastern Atlantic and impacts on gas phase uptake rates. *Atmospheric Chemistry and Physics*, 9:9299–9314, 2009.
- L. C. Anderson and D. W. Fahey. Studies with ClONO_2 : thermal dissociation rate and catalytic conversion to NO using an NO/O_3 chemiluminescence detector. *Journal of Physical Chemistry*, 94:644–652, 1990.
- R. Atkinson and J. Arey. Atmospheric degradation of volatile organic compounds. *Chemical Reviews*, 103(12):4605–4638, 2003.
- R. Atkinson, R. A. Cox, J. N. Crowley, R. F. Hampson, R. G. Hynes, M. E. Jenkin, J. A. Kerr, M. J. Rossi, and J. Troe. Summary of evaluated kinetic and photochemical data for atmospheric chemistry. Technical report, IUPAC Subcommittee on Gas Kinetic Data Evaluation for Atmospheric Chemistry, October 2006. URL <http://www.iupac-kinetic.ch.cam.ac.uk/>.
- A. R. Baker. Inorganic iodine speciation in tropical Atlantic aerosol. *Geophysical Research Letters*, 31:L23S02, 2004. doi: 10.1029/2004GL020144.
- A. R. Baker. Marine aerosol iodine chemistry: the importance of soluble organic iodine. *Environmental Chemistry*, 2:295–298, 2005.
- B. Ballesteros, N. R. Jensen, and J. Hjorth. FT-IR study of the kinetics and products of the reactions of dimethylsulphide, dimethylsulphoxide and dimethylsulphone with Br and BrO. *Journal of Atmospheric Chemistry*, 43(2):135–150, 2002.
- I. Barnes, J. Hjorth, and N. Mihalopoulos. Dimethyl sulfide and dimethyl sulfoxide and their oxidation in the atmosphere. *Chemical Reviews*, 106:940–975, 2006.
- D. L. Baulch, J. Duxbury, S. J. Grant, and D. C. Montague. Evaluated kinetic data for high-temperature reactions, Vol 4, - Homogeneous gas-phase reactions of halogen-containing and cyanide-containing species. *Journal of Physical and Chemical Reference Data*, 10(1):1–721, 1981.
- Y. Bedjanian, G. Le Bras, and G. Poulet. Rate constants for the reactions $\text{I} + \text{OCIO}$, $\text{I} + \text{ClO}$, $\text{Cl} + \text{I}_2$, and $\text{Cl} + \text{IO}$ and heat of formation of IO radicals. *Journal of Physical Chemistry*, 100:15130–15136, 1996.

- Y. Bedjanian, G. Le Bras, and G. Poulet. Kinetic study of the $\text{Br} + \text{IO}$, $\text{I} + \text{BrO}$ and $\text{Br} + \text{I}_2$ reactions. Heat of formation of the BrO radical. *Chemical Physics Letters*, 266(1-2):233–238, 1997.
- Y. Bedjanian, G. Le Bras, and G. Poulet. Kinetic study of the reactions $\text{Br} + \text{IBr} \rightarrow \text{I} + \text{Br}_2$ and $\text{I} + \text{Br}_2 \rightarrow \text{Br} + \text{IBr}$. *International Journal of Chemical Kinetics*, 30(12):933–940, 1998a.
- Y. Bedjanian, G. Le Bras, and G. Poulet. Kinetics and mechanism of the $\text{IO} + \text{BrO}$ reaction. *Journal of Physical Chemistry A*, 102:10501–10511, 1998b.
- Y. Bedjanian, G. Laverdet, and G. Le Bras. Low-pressure study of the reaction of Cl atoms with isoprene. *Journal of Physical Chemistry A*, 102(6):953–959, 1998c.
- W. J. Bloss, D. M. Rowley, R. A. Cox, and R. L. Jones. Kinetics and products of the IO self-reaction. *Journal of Physical Chemistry*, 105:7840–7854, 2001.
- E. N. Chesnokov. Application of IR-chemiluminescence method for determination of rate constants of bimolecular reactions which are not leading to the formation of excited products. *Khimicheskaya Fizika*, 10(2):204 – 212, 1991.
- M. A. A. Clyne and H. W. Cruse. Atomic resonance fluorescence spectrometry for the rate constants of rapid bimolecular reactions. Part 2: reactions $\text{Cl} + \text{BrCl}$, $\text{Cl} + \text{Br}_2$, $\text{Cl} + \text{ICl}$, $\text{Br} + \text{IBr}$, $\text{Br} + \text{ICl}$. *Faraday Transactions*, 68:1377–1387, 1972.
- M. A. A. Clyne, P. B. Monkhouse, and L. W. Townsend. Reactions of O^3P atoms with halogens - rate constants for elementary reactions $\text{O} + \text{BrCl}$, $\text{O} + \text{Br}_2$, and $\text{O} + \text{Cl}_2$. *International Journal of Chemical Kinetics*, 8(3):425–449, 1976.
- E. S. N. Cotter, N. J. Booth, C. E. Canosa-Mas, D. J. Gray, D. E. Shallcross, and R. P. Wayne. Reactions of Cl atoms with CH_3I , $\text{C}_2\text{H}_5\text{I}$, 1 – $\text{C}_3\text{H}_7\text{I}$, 2 – $\text{C}_3\text{H}_7\text{I}$ and CF_3I : kinetics and atmospheric relevance. *Physical Chemistry Chemical Physics*, 3:402–408, 2001.
- E. S. N. Cotter, C. E. Canosa-Mas, C. R. Manners, R. P. Wayne, and D. E. Shallcross. Kinetic study of the reactions of OH with the simple alkyl iodides: CH_3I , $\text{C}_2\text{H}_5\text{I}$, 1- $\text{C}_3\text{H}_7\text{I}$ and 2- $\text{C}_3\text{H}_7\text{I}$. *Atmospheric Environment*, 37:1125–1133, 2003.
- V. Damian, A. Sandu, M. Damian, F. Potra, and G. R. Carmichael. The kinetic pre-processor KPP - A software environment for solving chemical kinetics. *Computers and Chemical Engineering*, 26:1567–1579, 2002.

- T. J. Dillon, M. E. Tucceri, and J. N. Crowley. Laser induced fluorescence studies of iodine oxide chemistry. Part II: the reactions of IO with CH_3O_2 , CF_3O_2 and O_3 . *Physical Chemistry Chemical Physics*, 8:5185–5198, 2006.
- D. A. Dolson and S. R. Leone. A reinvestigation of the laser-initiated Cl_2/HBr chain-reaction. *Journal of Physical Chemistry*, 91(13):3543–3550, 1987.
- J. S. Francisco and J. N. Crowley. Theoretical investigation of product channels in the $\text{CH}_3\text{O}_2 + \text{Br}$ reaction. *Journal of Physical Chemistry A*, 110:3778–3784, 2006.
- J. C. Gómez-Martín, P. Spietz, and J. P. Burrows. Kinetic and mechanistic studies of the I_2/O_3 photochemistry. *Journal of Physical Chemistry A*, 111(2):306–320, 2007.
- J. C. Hansen, Y. M. Li, J. S. Francisco, and Z. J. Li. On the mechanism of the $\text{BrO} + \text{CH}_2\text{O}$ reaction. *Journal of Physical Chemistry A*, 103(42):8543–8546, 1999.
- A. Jefferson, J. M. Nicovich, and P. H. Wine. Temperature dependent kinetics studies of the reactions $\text{Br}(^2\text{P}_{3/2}) + \text{CH}_3\text{SCH}_3 \longleftrightarrow \text{CH}_3\text{SCH}_2 + \text{HBr}$. Heat of formation of the CH_3SCH_2 radical. *Journal of Physical Chemistry*, 98:7128–7135, 1994.
- M. E. Jenkin, R. A. Cox, A. Mellouki, G. Le Bras, and G. Poulet. Kinetics of the reaction of iodine atoms with HO_2 radicals. *Journal of Physical Chemistry*, 94(7):2927–2934, 1990.
- N. Kaltsoyannis and J. M. C. Plane. Quantum chemical calculations on a selection of iodine-containing species (IO , OIO , INO_3 , $(\text{IO})_2$, I_2O_3 , I_2O_4 and I_2O_5) of importance in the atmosphere. *Physical Chemistry Chemical Physics*, 10:1723–1733, 2008.
- W. C. Keene, M. S. Long, A. A. P. Pszenny, R. Sander, J. R. Maben, A. J. Wall, T. L. O’Halloran, A. Kerkweg, E. V. Fischer, and O. Schrems. Latitudinal variation in the multiphase chemical processing of inorganic halogens and related species over the eastern North and South Atlantic Oceans. *Atmospheric Chemistry and Physics*, 9:7361–7385, 2009.
- O. Kondo and S. W. Benson. Kinetics and equilibria in the system $\text{Br} + \text{CH}_3\text{OOH}$ reversible $\text{HBr} + \text{CH}_3\text{OO}$ - an upper limit for the heat of formation of the methylperoxy radical. *Journal of Physical Chemistry*, 88(26):6675–6680, 1984.

- A. Kukui, U. Kirchner, T. Benter, and R. N. Schindler. A gas kinetic investigation of HOBr reactions with CI(2P), O(3P) and OH(2II). The reaction of BrCl with OH(2II). *Physical Chemistry Chemical Physics*, 100(4):455–461, 1996.
- A. Kukui, D. Borissenko, G. Laverdet, and G. Le Bras. Gas-phase reactions of OH radicals with dimethyl sulfoxide and methane sulfinic acid using turbulent flow reactor and chemical ionization mass spectrometry. *Journal of Physical Chemistry A*, 107(30):5732–5742, 2003.
- M. J. Lawler, B. D. Finley, W. C. Keene, A. A. P. Pszenny, R. von Glasow, and E. S. Saltzman. Pollution-caused enhancement of Cl chemistry in the eastern tropical Atlantic boundary layer. *Geophysical Research Letters*, 36:L08810, 2009. doi: 10.1029/2008GL036666.
- M. J. Lawler, R. Sander, L. J. Carpenter, J. D. Lee, R. von Glasow, R. Sommariva, and E. S. Saltzman. HOCl and Cl₂ observations in marine air. *Atmospheric Chemistry and Physics*, 11(15):7617–7628, 2011. URL www.atmos-chem-phys.net/11/7617/2011/.
- H. Leser, G. Hönninger, and U. Platt. MAX-DOAS measurements of BrO and NO₂ in the marine boundary layer. *Geophysical Research Letters*, 30(10):1537, 2003. doi: 10.1029/2002GL015811.
- L. M. Loewenstein and J. G. Anderson. Rate and product measurements for the reactions of OH with I₂ and ICl at 298K: separation of gas-phase and surface reaction components. *Journal of Physical Chemistry*, 89(25):5371–5379, 1985.
- A. S. Mahajan, J. M. C. Plane, H. Oetjen, L. Mendes, R. W. Saunders, A. Saiz-Lopez, C. E. Jones, L. J. Carpenter, and G. B. McFiggans. Measurements and modelling of tropospheric reactive halogen species over the tropical Atlantic Ocean. *Atmospheric Chemistry and Physics*, 10:4611–4624, 2010.
- M. Martin, D. Pöhler, K. Seitz, R. Sinreich, and U. Platt. BrO measurements over the Eastern North-Atlantic. *Atmospheric Chemistry and Physics*, 9:9545–9554, 2009.
- K. Müller, S. Lehmann, D. van Pinxteren, T. Gnauk, N. Niedermeier, A. Wiedensohler, and H. Herrmann. Particle characterization at the Cape Verde atmospheric observatory during the 2007 RHaMBLe intensive. *Atmospheric Chemistry and Physics*, 10:2709–2721, 2010.
- J. J. Orlando and G. S. Tyndall. Rate coefficients for the thermal decomposition of BrONO₂ and the heat of formation of BrONO₂. *Journal of Physical Chemistry*, 100:19398–19405, 1996.

- H. D. Osthoff, M. J. Pilling, A. R. Ravishankara, and S. S. Brown. Temperature dependence of the NO_3 absorption cross-section above 298 K and determination of the equilibrium constant for $\text{NO}_3 + \text{NO}_2 \longleftrightarrow \text{N}_2\text{O}_5$ at atmospherically relevant conditions. *Physical Chemistry Chemical Physics*, 9:5785–5793, 2007.
- S. Pechtl and R. von Glasow. Reactive chlorine in the marine boundary layer in the outflow of polluted continental air: a model study. *Geophysical Research Letters*, 34:L11813, 2007. doi: 10.1029/2007GL029761.
- S. Pechtl, G. Schmitz, and R. von Glasow. Modelling iodide-iodate speciation in atmospheric aerosol: contributions of inorganic and organic iodine chemistry. *Atmospheric Chemistry and Physics*, 7:1381–1393, 2007.
- J. M. C. Plane, D. M. Joseph, B. J. Allan, S. H. Ashworth, and J. S. Francisco. An experimental and theoretical study of the reactions $\text{OIO} + \text{NO}$ and $\text{OIO} + \text{OH}$. *Journal of Physical Chemistry*, 110:93–100, 2006.
- A. R. Ravishankara, E. J. Dunlea, M. A. Blitz, T. J. Dillon, D.E. Heard, M. J. Pilling, R. S. Strekowski, J. M. Nicovich, and P.H. Wine. Redetermination of the rate coefficient for the reaction of $\text{O}(^1\text{D})$ with N_2 . *Geophysical Research Letters*, 29(15):1745, 2002. doi: 10.1029/2002GL014850.
- K. A. Read, A. S. Mahajan, L. J. Carpenter, M. J. Evans, B. V. E. Faria, D. E. Heard, J. R. Hopkins, J. D. Lee, S. J. Moller, A. C. Lewis, L. Mendes, J. B. McQuaid, H. Oetjen, A. Saiz-Lopez, M. J. Pilling, and J. M. C. Plane. Extensive halogen-mediated ozone destruction over the tropical Atlantic Ocean. *Nature*, 453:1232–1235, 2008.
- V. Riffault, Y. Bedjanian, and G. Poulet. Kinetic and mechanistic study of the reactions of OH with IBr and HOI. *Journal of Photochemistry and Photobiology A - Chemistry*, 176:155–161, 2005.
- S. P. Sander, R. R. Friedl, A. R. Ravishankara, D. M. Golden, C. E. Kolb, M. J. Kurylo, M. J. Molina, G. K. Moortgat, H. Keller-Rudek, B. J. Finlayson-Pitts, P. H. Wine, R. E. Huie, and V. L. Orkin. Chemical kinetics and photochemical data for use in atmospheric studies. evaluation no. 15. Technical report, NASA JPL Panel for Data Evaluation, July 2006. URL <http://jpldataeval.jpl.nasa.gov/>.
- R. W. Saunders and J. M. C. Plane. Formation pathways and composition of iodine oxide ultra-fine particles. *Environmental Chemistry*, 2:299–303, 2005.

- S. M. Saunders, M. E. Jenkin, R. G. Derwent, and M. J. Pilling. Protocol for the development of the Master Chemical Mechanism, MCM v3 (Part A): tropospheric degradation of non-aromatic volatile organic compounds. *Atmospheric Chemistry and Physics*, 3(1):161–180, 2003.
- R. Sommariva, W. J. Bloss, and R. von Glasow. Uncertainties in gas-phase atmospheric iodine chemistry. *Atmospheric Environment*, 2012.
- K. Toyota, Y. Kanaya, M. Takahashi, and H. Akimoto. A box model study on photochemical interactions between VOCs and reactive halogen species in the marine boundary layer. *Atmospheric Chemistry and Physics*, 4:1961–1987, 2004.
- A. A. Turnipseed, S. B. Barone, and A. R. Ravishankara. Reaction of OH with dimethyl sulfide. 2. Products and mechanism. *Journal of Physical Chemistry*, 100:14703–14713, 1996.
- G. S. Tyndall, R. A. Cox, C. Granier, R. Lesclaux, G. K. Moortgat, M. J. Pilling, A. R. Ravishankara, and T. J. Wallington. Atmospheric chemistry of small organic peroxy radicals. *Journal of Geophysical Research*, 106(D11):12157–12182, 2001.
- H. van den Bergh and J. Troe. Kinetic and thermodynamic properties of INO and INO₂ intermediate complexes in iodine recombination. *Journal of Chemical Physics*, 64(2):736–742, 1976.
- R. von Glasow, R. Sander, A. Bott, and P. J. Crutzen. Modeling halogen chemistry in the marine boundary layer - 1. Cloud-free MBL. *Journal of Geophysical Research*, 107(D17):4341, 2002a. doi: 10.1029/2001JD000942.
- R. von Glasow, R. Sander, A. Bott, and P. J. Crutzen. Modeling halogen chemistry in the marine boundary layer - 2. Interactions with sulfur and the cloud-covered MBL. *Journal of Geophysical Research*, 107(D17):4323, 2002b. doi: 10.1029/2001JD000943.
- F. D. Yin, D. Grosjean, and J. H. Seinfeld. Photooxidation of dimethyl sulfide and dimethyl disulfide - 1. Mechanism development. *Journal of Atmospheric Chemistry*, 11(4):309–364, 1990a.
- F. D. Yin, D. Grosjean, R. C. Flagan, and J. H. Seinfeld. Photooxidation of dimethyl sulfide and dimethyl disulfide - 2. Mechanism evaluation. *Journal of Atmospheric Chemistry*, 11(4):365–399, 1990b.